

The Theory and Application of Bimetallic Electrode Systems in Electrometric Analysis

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

By

Florence Fenwick

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EASTON, PA.:
ESCHENBACH PRINTING COMPANY
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FLORENCE FENWICK

PART I

THEORY AND DEVELOPMENT

BIMETALLIC ELECTRODE SYSTEMS IN ELECTROMETRIC ANALYSIS. I. SYSTEMS COMPRISING TWO DISSIMILAR METALS

Introduction

A large amount of investigation has been made during the past 10 years on the extension of the use of the electrometric indicator in volumetric analysis and the simplification of the apparatus required for potentiometric work. In connection with the latter, various changes have been suggested both for the measuring instruments employed¹ and the electrode arrangement used. Kolthoff² has classified the electrode systems used in electrometric analysis under the following three heads. (1) The system ordinarily used, consisting of an unattackable metal electrode and a constant half-cell, usually a calomel reference electrode. (2) The Pinkhof system, in which the calomel electrode is replaced by a compensation electrode the potential of which is exactly equal to that of the unattackable electrode-solution at the completion of the titration. The end-point is marked by a reversal of polarity. The arrangement has a number of disadvantages. Every titration has its peculiar electrode system, there is no warning of the approach to the end-point, and it is difficult to compensate for the effects of concentration and foreign salts. (3) The Treadwell system. W. D. Treadwell uses, in place of a standard electrode, a half-cell which contains a solution of the same composition as the solution titrated at its end-point, in contact with a second unattackable electrode. The disadvantage here is the specific character of any one arrangement.

The idea of using bimetallic systems in electrometric analysis was suggested by Hostetter and Roberts³ in connection with the titration of iron in small quantities. Because of the practical absence of a break at the end-point in the titration of ferrous sulfate with 0.1 N potassium dichromate when palladium replaced the usual platinum electrode, Hostetter and Roberts called attention to the possibility of substituting a palladium electrode for the calomel reference electrode.

Preliminary Investigation of Bimetallic Systems

Palladium

Such a means of simplifying the usual apparatus seemed distinctly worth following up, so we attempted first to verify the results of these

¹ Hildebrand, *J. Am. Chem. Soc.*, **35**, 869 (1913). Forbes and Bartlett, *ibid.*, **35**, 1527 (1913). Kelley and Conant, *ibid.*, **38**, 341 (1916). Kelley, Adams and Wiley, *J. Ind. Eng. Chem.*, **9**, 780 (1917). Roberts, *J. Am. Chem. Soc.*, **41**, 1358 (1919). Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 680 (1919). Goode, *J. Am. Chem. Soc.*, **44**, 26 (1922).

² Kolthoff, *Chem Weekblad*, **50**, 659 (1920).

³ Hostetter and Roberts, *J. Am. Chem. Soc.*, **41**, 1343, footnote 1 (1919).

authors in the titration of solutions of higher iron content. Fig. 1 shows the results of the titration of 75 cc. of a solution of ferrous

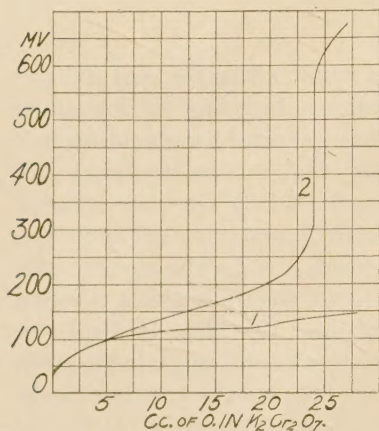


Fig. 1.

sulfate approximately 0.033 N and containing a high concentration of hydrochloric acid. Curve 1 is the curve of the system, Pd-Titrated Soln.-0.1 N KCl, HgCl—Hg, and Curve 2 of the system, Pt-Titrated Soln.-0.1N KCl, HgCl—Hg. The platinum electrode was a piece of pure platinum wire 46 mm. long and 0.49 mm. in diameter. The palladium electrode was a thin strip of foil about 5 mm. wide and 10 mm. long. The difference in behavior of the 2 metals at the end-point is obvious. Upon substituting the palladium electrode for the calomel an extremely sharp but transient end-point was obtained. In order to investigate further the fleeting character of this end-point, the palladium and calomel electrodes were connected in the circuit through a double-throw switch so that at any point during the course of the titration the potential of the platinum electrode against both the calomel and palladium might be measured. The results are shown graphically in Fig. 2. The solution contained 25.00 cc. of 0.1092 N ferrous sulfate and 50 cc. of hydrochloric acid, sp. gr. 1.18, in a total volume of 75 cc. Curve 1 is the Pt-Pd curve, Curve 2 is the Pt-calomel. The first sharply defined break came after the calculated end-point and the voltage fell almost instantaneously to its former value with both reference electrodes. The addition of 0.1cc. portions of potassium dichromate caused a sharp rise followed by a slow falling of the potential until there was 0.7 cc. of dichromate in excess of the calculated amount. At this point there was no fall, but rather a slow rise for the observed space of 4 minutes. Since the end-point behavior was the same with both electrode systems it is apparent

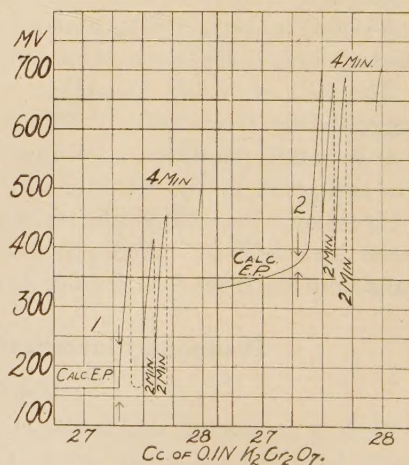


Fig. 2.

that variable voltage effects are not due to any property of the metallic palladium but the cause of the difficulty must lie in the solution itself. The fact that the first fleeting break occurred in the presence of a supposed excess of the oxidizing agent indicated that the titrated solution contained other reducing agents than the known amount of ferrous iron. This could mean only that the palladium electrode was attacked. To verify this conclusion, titrations were carried out to the first sharp break with solutions of different acid concentration and palladium electrodes of varying surface exposure, the other electrode being pure platinum. The results are recorded in Table I. In this, and all other tables, the concentration of acid in the solution is expressed as percentage by volume of sulfuric acid, sp. gr. 1.84, or of hydrochloric acid, sp. gr. 1.18.

TABLE I

TITRATION OF FERROUS IRON WITH PLATINUM-PALLADIUM ELECTRODES

The solutions titrated contained 25.00 cc. of approximately 0.1 *N* ferrous sulfate in an initial volume of 75 cc. The oxidizing agent was 0.1 *N* potassium dichromate. The time required for the titration was 5 minutes except in the fifth experiment when it was 25 minutes

Length of electrode Mm.	Acid conc. % HCl	Error 0.1 <i>N</i> K ₂ Cr ₂ O ₇ Cc.	Character of end-point
10	66	+0.30	Good
	33	+0.30	Good
	13	+0.30	Good
	4	+0.30	Poor
	66	1.00	Good
	Any Conc. H ₂ SO ₄		Poor
8	66	+0.26	Good
4	66	+0.12	Fair
Point	66	...	None

Although the error was considerably reduced by decreasing the surface exposure of the palladium electrode and the time required for the titration, it was not found possible to reduce it to within acceptable limits. A mere point contact electrode gave no results and the use of a weakly acid solution of hydrochloric acid or sulfuric acid of any strength was unsatisfactory. Apparently the difference in voltage of the systems, Pt-FeSO₄-Pd and Pt-Fe₂(SO₄)₃-Pd, is insufficient for the appearance of a sharp break, and it is only by virtue of the presence of some palladous ion that this occurs. At the same time, some reduction of the ferric salt occurs and an excess of the oxidizing agent must, therefore, be used.

In spite of the unsatisfactory results obtained with pure palladium it seemed possible that a dilution of the palladium in the electrode might decrease the error in the titration to a negligible amount for analytical

purposes. Hostetter and Roberts³ found a very appreciable break with a gold electrode in the dichromate titration of ferrous sulfate but not nearly as good as with clean platinum. Alloys of gold and palladium of small surface exposure and containing variable proportions of the constituents were, therefore, tried, with the same platinum electrode used before. The results were irregular and much too high.

To complete the work with palladium, a platinum-palladium alloy was made and comparative titrations run using as reference electrodes

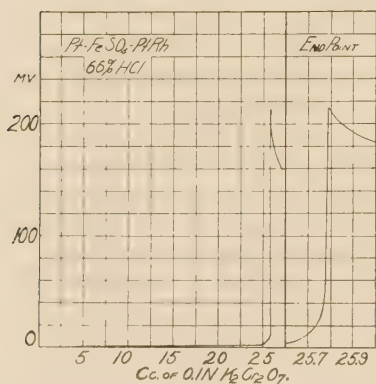


Fig. 3.

with platinum pure palladium wire 1 mm. in diameter, 7 mm. long, and the alloy. The oxidizing agent was added as rapidly as possible and the electrodes were not in contact with the solution for more than 3 minutes during each titration. The palladium wire was a more compact form of the metal than the foil used previously and the error was very appreciably reduced. It seemed reasonable to conclude from these later results that under carefully regulated conditions palladium and platinum-palladium may be employed as electrodes

with reasonable accuracy. Irregularities persisted, however, to a considerable extent. The palladium wire showed visible signs of attack after some 50 titrations. It seemed advisable, therefore, to investigate thoroughly other metals less easily attacked, especially those of the platinum group, with a view to finding a bimetallic system capable of giving more regular results.

Platinum and Rhodium

The first new combination tried was that of pure platinum with platinum-rhodium thermocouple wire. Fig. 3 gives the titration curve of this system with potassium dichromate.

TABLE II
TITRATION OF FERROUS IRON WITH ELECTRODES OF PLATINUM
AND PLATINUM-RHODIUM

Electrode system	Acidity %HCl by volume	0.1 N $K_2Cr_2O_7$		0.1 N $KMnO_4$	
		Average error	Average break	Average error	Average break
		Cc.	Mv.	Cc.	Mv.
Pt-PtRh	66	-0.12	104	+0.18	20
	50	0.00	97	+0.08	49
	33	0.00	48	-0.05	40
	20	+0.01	32	+0.01	29

	13	0.00	47	0.00	69
	6	-0.02	26	+0.06	38
	26 H ₂ SO ₄	0.00	105		..
Pt-AgCl	20 H ₂ SO ₄		...	-0.03	334
	66		...	-0.21	298
	50		...	+0.01	204
	33		...	0.00	304
PtRh-AgCl	33		...		237

The results of a number of titrations are given in Table II. All solutions contained 25.00 cc. of approximately 0.1 *N* ferrous sulfate. The error in the case of the dichromate titrations is based on the electrometric standardization with platinum and silver chloride electrodes.⁴ The visual end-point standardization is used in the case of permanganate titrations.

There are some differences between the dichromate and the permanganate titrations, rather more in degree than in character, which will be brought out later. Fig. 5 is the curve of the permanganate titration in 20% sulfuric acid, using a platinum-platinum-rhodium system.

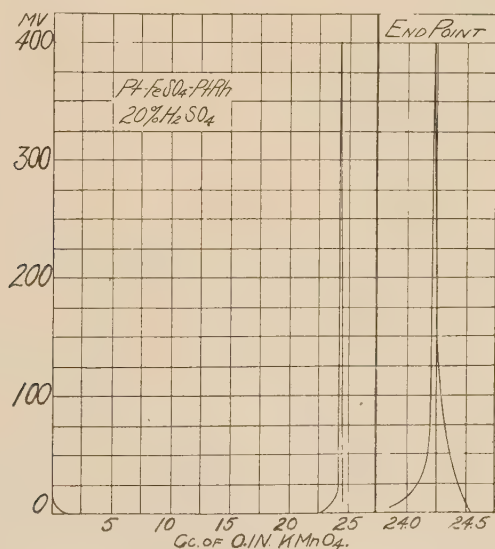


Fig. 5.

Tungsten

Because of its high resistance to acids, tungsten seemed to offer a promising electrode material. A piece of tungsten wire 2 mm. in diameter was used as electrode in a number of titrations, the results of which are

⁴ See footnote 4 on page 12.

recorded in Table III. Twenty-five cc. of 0.1 *N* FeSO₄ was used in each case, as before.

TABLE III
TITRATION OF FERROUS IRON WITH ELECTRODES OF PLATINUM, PLATINUM-
RHODIUM AND TUNGSTEN

Electrode system	Acidity	0.1 <i>N</i> K ₂ Cr ₂ O ₇		0.1 <i>N</i> KMnO ₄	
		Average error	Average break	Average error ^a	Average break
	% Acid	Cc.	Mv.	Cc.	Mv.
Pt-W	50 HCl	+0.02	31	-0.04	76
	33 HCl	0.00	34	-0.05	176
	20 HCl		...	-0.05	100
	20 H ₂ SO ₄		...	-0.04	252
	13 H ₂ SO ₄	-0.02	14	-0.03	81
W-AgCl	50 HCl	No end-point		No end-point	
	20 H ₂ SO ₄				
PtRh-W	33 HCl	-0.01	72	-0.02	320
	20 H ₂ SO ₄	-0.04	101	-0.04	494

^a Based on visual end-point.

The curves in the region of the end-point for both dichromate and permanganate titrations with platinum and tungsten electrodes are shown in Fig. 6. According to the above tabulation there is no determinable break with tungsten-silver-chloride combinations. This is clearly shown by Curve 1, Fig. 7, which is the end-point curve for permanganate titra-

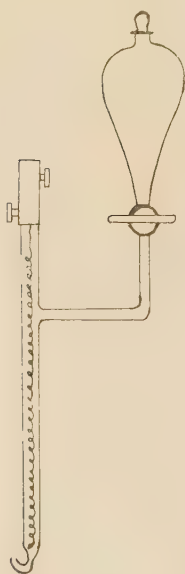


Fig. 4.

⁴ For all titrations requiring a constant half-cell, the silver chloride electrode was found much superior to the calomel. Four electrodes were made up as described by MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1449 (1915), except that a coil of silver wire replaced the platinum gauze used by these authors. The wire was plated with silver from a cyanide bath, coated with silver chloride by making it the anode in a solution of sodium chloride, and placed in 0.1 *N* potassium chloride in the container shown in Fig. 4.

The reservoir was a 20cc. dropping funnel. The great advantage of this type of holder is the comparatively negligible resistance offered by the short column of liquid intervening between the titrated solution and the metal of the electrode.

The potential of each of the electrodes made was measured against a 0.1 *N* calomel electrode and the difference found to be 0.045 volt in every case. Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2252 (1917), obtained the value 0.046 volt. After several months of severe and continuous use the potential of one of the electrodes was again measured. There was no appreciable change. Although the silver chloride does not possess the high degree of reproducibility of the calomel, it is more rugged, comes more quickly to equilibrium, and the potential of single elements is more constant than with the latter.

tions of ferrous sulfate in 20% sulfuric acid and Curve 2 for dichromate titrations in 33% hydrochloric acid.

Quantitatively considered the results in Tables II and III are decidedly encouraging. In 66% hydrochloric acid too little oxidizing agent was required probably due to oxidation by the air.⁵ (See Table II.) With an acidity of 50% or less the results are very satisfactory. The permanganate titration of ferrous sulfate solutions containing free sulfuric acid gave results slightly below the visual end-point. The

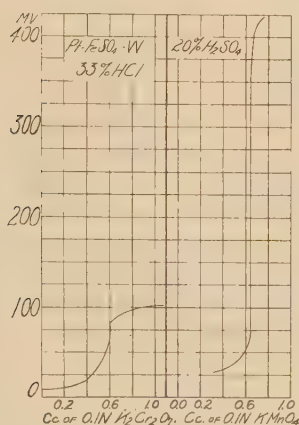


Fig. 6.

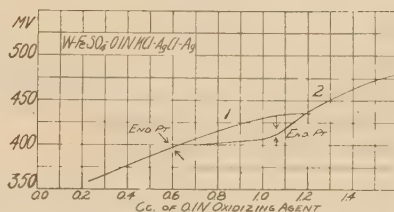


Fig. 7.

difference is quite small enough to be accounted for by the excess of the oxidizing agent required for the visual end-point. In hydrochloric acid solution the amount of permanganate required with the platinum-platinum-rhodium system is somewhat greater than in dil. sulfuric acid. This difference is not great, but since the palladium electrode was found to be very appreciably attacked under similar conditions, especially in the presence of an increased iron content, it seemed advisable to investigate further the error involved here. The iron content of the solutions was increased by the addition of a strong solution of ferric chloride (1 cc. = 0.086 g. of iron) in which the ferrous iron had been carefully determined electrometrically by titration with 0.01 *N* potassium dichromate and 0.001 *N* potassium permanganate solutions (29.07 cc. of ferric chloride = 2.50 g. of iron and contained 0.36 cc. 0.1 *N* ferrous iron). The results of a number of titrations are given in Table IV.

⁵ Eppley and Vosburgh, *J. Am. Chem. Soc.*, **44**, 2148 (1922), found the opposite effect using the reverse titration, in which oxidation by the air would not occur.

TABLE IV

TITRATION OF FERROUS IRON WITH PERMANGANATE IN HYDROCHLORIC ACID
SOLUTIONS CONTAINING MUCH FERRIC IRON

In all cases the acid concentration was 33% by volume of hydrochloric acid, sp. gr. 1.18. The total iron was 0.14 g. in the third experiment and 2.64 g. in all others

Electrode system	MnSO ₄ (cryst.)	Average break	Error in 0.1 N KMnO ₄
	G.	Mv.	Cc.
Pt-AgCl	None	186	+0.03
	5	172	0.00
Pt-PtRh	None	27	+0.02
	None	17	+0.07
	5	46	-0.02
Pt-W	None	182	+0.07
	5	170	+0.03

The error is brought well within allowable limits by the addition of manganous sulfate even in solutions high in iron. It is apparently due to a very slight decomposition of the hydrochloric acid, liberating chlorine. The results show that the electrometric method gives a means of titrating strong hydrochloric acid solutions of ferrous iron with permanganate.

Summary of Preliminary Investigation

A number of electrode combinations other than those already described were investigated. An attempt has been made to tabulate the main features of all the combinations in Table V. Unless otherwise specified the solutions titrated contained 25.00 cc. of an approximately 0.1 *N* ferrous sulfate solution in an initial volume of 75 cc., 20% by volume of conc. sulfuric or 33% conc. hydrochloric acid.

TABLE V

PRELIMINARY INVESTIGATIONS

Electrode system	Millivolts Break				Remarks
	0.1 <i>N</i> K ₂ Cr ₂ O ₇		0.1 <i>N</i> KMnO ₄		
	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	
Pt-AgCl	52 (fair)	24 (poor)	216 (excel.)	304 (excel.)	See footnote ^a
W-Pt	14 (13% acid)	34 (Downward crawl)	252	176	
W-AgCl	No definite end-point				
Mo-	No end-point with any combination, attacked too rapidly.				Ta is comparable with W but the break is always less.
Ta-Pt		20	150		

Ta-AgCl		No end-point			
PtRh-Pt	95	48	357	40	Tendency to give high results in HCl soln. with KMnO_4 reduced to 0.01 cc. by addition of MnSO_4 .
			(sharp fall with slight excess)	(no fall with excess)	
PtRh-AgCl	91	64	139	237	
PtRh-W	101	72	494	320	
Rh-Pt	67	63	248	206	The reducing action of Pd and PtPd too rapid to permit of the practical use of either as an electrode.
Rh-AgCl	no e.-p.	no e.-p.	12	(no sharp break)	
Rh-W	no e.-p.	no e.-p.	no e.-p.	35	
				(poor)	
PtPd-Pt	28	34	132	171	The reducing action of Pd and PtPd too rapid to permit of the practical use of either as an electrode.
PtPd-AgCl	66	23	(downward crawl)	58	
				(crawl)	
PtPd-W	71	39	860	62	
Pd-Pt	33	97	208	163	Alloy 10.5% Ir.
		(50% acid)		(20% acid)	
Pd-AgCl	64	no e.-p.	145	no e.-p.	
		(13% acid)	(13% acid)		
Pd-W	35	no e.-p.	98	no e.-p.	See footnote ^b
		(attacked)		(attacked)	
PtIr-Pt	70	75	110	56	
			(fall with excess)	(fall with excess)	
PtIr-AgCl	34	60	100	162	The natural irid-osmium alloy
			(large rise with excess)	(large rise with excess)	
PtIr-W	25	65	150	150	
			(large rise with excess)		
Ir-Pt	low (sensitive)	33	312	130	
			(fall with excess)	(fall with excess)	
Ir-AgCl	68	54	55	72	
			(large rise with excess)	(large rise with excess)	
Ir-W	28	43	207	323	
PtOs-Pt	50	33	157	205	
			(fall with excess)	(fall with excess)	
PtOs-AgCl	70	69	372	287	
PtOs-W	40	59	380	177	
IrOs-Pt		15	400	150	
IrOs-Ir	22	52	309	242	
PtAu-Pt	35	26	86	225	
			(fall with excess)		

TABLE V (Continued)

Electrode system	Millivolts Break				Remarks
	0.1 N K ₂ Cr ₂ O ₇		0.1 N KMnO ₄		
	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	
PtAu-AgCl	57	26	185	59	
PtAu-W	30	36	280	65	
Pt-Pt			150 ^c		Feb. 13, 1920
Pt-Pt	no e.-p.	no e.-p.	not > 5		Feb. 14, 1920

^a The magnitude of the break in HCl solution with $K_2Cr_2O_7$ is materially influenced by the condition of the Pt and the acidity of the solution. A freshly ignited electrode gives the best results and increased acidity makes the break both sharper and greater. Above 50% HCl the results obtained are low. Increased concentration of Fe causes a decrease in the break.

Theoretical results are obtained by titrating with $KMnO_4$ in H_2SO_4 solution. In HCl the tendency is to run high, usually 0.05–0.12 cc. Later titrations with concentrations of Fe to 2.64 g. seemed to show this error independent of the concentration of both Fe and HCl, provided the latter is not above 50%. The addition of 5 g. of $MnSO_4$ reduced this error to 0.05 cc.

^b $KMnO_4$ titrations with both Ir and PtIr against AgCl seemed to be characterized by a very large break with one drop excess. The break at the end-point is sharp and the larger break immediately following is sometimes 4 times the value of the smaller. The primary break was demonstrated to be the real end-point by comparative titrations with other systems.

^c Identical electrodes cut from foil and sealed in glass. Apparently a strained condition existed in the freshly sealed-in electrodes which caused the break. Successive titrations dissipated this strain, an indication that the end-point with bimetallic systems is a polarization phenomenon.

Characteristics of Bimetallic Systems

The actual magnitude of the end-point break is usually less than when a constant half-cell is used with only one metal electrode. However, in the latter case, even under the most favorable circumstances, the break with dichromate little more than equals the total rise from the beginning of the titration to the end-point and it is often much less. With 2 metal electrodes the initial voltage, with zero quantity of the higher stage of oxidation present, varies considerably according to the pre-treatment of the electrodes and the condition of the solution as to concentration, acidity, and foreign salts. Upon the addition of the oxidizing agent the voltage falls rapidly to practically zero and remains at this value until the titration is within 0.2 – 0.3 cc. of the end-point. A slight rise then gives warning of the approaching end-point which occurs with greater sharpness than with the usual electrode combination. The total rise throughout the entire course of the titration is so entirely negligible as compared with the abrupt change at the end-point that this latter is unmistakable. With bimetallic combinations in which tungsten forms one

electrode there is a slow, continuous rise throughout the course of the titration comparable to the rise with monometallic systems but rarely amounting to 50 millivolts prior to the end-point.

The conditions in the presence of an excess of the oxidizing agent are interesting. Fig. 3 shows a slight fall in voltage in excess of potassium dichromate with Pt-PtRh electrodes. This fall is not always found under similar circumstances; sometimes the voltage remains constant after the break or, at most, there may be a very slight rise. With permanganate titrations in sulfuric acid the behavior is much more marked (Fig. 5). 0.02 cc. in excess is sufficient to cause a fall in voltage which may equal more than $\frac{3}{4}$ the total rise at the end-point. Continued addition of permanganate causes a still further decrease but with lessening velocity as the potential approaches its former zero value. This behavior with excess of the oxidizing agent may be a disadvantage. When titrations are being carried out in colored solutions which veil the visual end-point, if the operator has approached the end-point so rapidly as not to observe the slight rise preceding it, he may overstep it and be unaware of the fact for some time. In hydrochloric acid solutions the break is not nearly as good as in sulfuric, sometimes only a tenth of the magnitude of the latter, but it is sharp. The fall in excess is not as marked as in the latter case and may not occur at all. It must be pointed out that the phenomenal fall applies only in the case of bimetallic systems of metals and alloys of the platinum group. Combinations including tungsten never behave thus, although the potential may "crawl" somewhat here.

Analysis of the End-point Phenomenon

Bancroft⁶ long ago pointed out that the e.m.f. of oxidation cells is an additive property and the potential of a single cell the difference between 2 single electrode potentials. The attempt was therefore made to show the part played by each electrode in bimetallic systems.

For this purpose the 2 metal electrodes and a standard silver chloride half-cell were immersed in the solution to be titrated and connected in the circuit through a small set of mercury switches in such a way that the potential of any one of the 3 possible electrode combinations was readily obtained at any stage of the titration. It is obvious that the difference between the potential of the combinations Metal 1-AgCl and Metal 2-AgCl must equal that of the system Metal 1-Metal 2 and, therefore, is a check on the accuracy of the latter measurement. Fig. 8 gives the single electrode potential curves of platinum solution and tungsten solution.

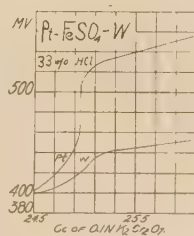


Fig. 8.

⁶ Bancroft, *Z. physik. Chem.*, 10, 387 (1892).

Fig. 9 shows the corresponding curves for platinum-platinum-rhodium under the same conditions.

The last two figures illustrate very clearly the functions of the individual electrodes. Initially, with only ferrous iron present, the relation of the 2 metals to the solution is different, resulting in an appreciable potential difference. Addition of the oxidizing agent decreases this difference which now falls rapidly to zero. As the end-point is approached the electrodes again begin to function differently and just as the last trace of ferrous ion disappears there is a sharp change in the relative electrode conditions. It may be mentioned here that the electrodes do not always behave the same from one titration to another. The break is always present and does not alter in location but its magnitude varies considerably. Sometimes one metal may be the positive electrode, sometimes

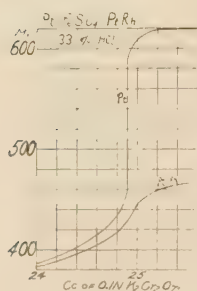


Fig. 9.

the other, depending largely upon their pre-treatment. The electrodes used in the titration represented by Fig. 8 had been freshly treated with boiling chromic acid. After such treatment platinum is normally positive to the alloy, but the difference decreases with successive titrations and conditions may often reverse. With tungsten there is never a reversal of polarity. The platinum metals and their mutual alloys are invariably positive to tungsten when equilibrium has been established although the magnitude of the break at the end-point alters very appreciably.

The conditions in the case of the permanganate titration of ferrous sulfate with platinum-platinum-rhodium electrodes in sulfuric acid solution are given in Fig. 10.

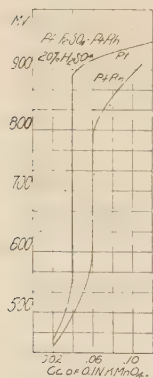


Fig. 10.

The break with the platinum-rhodium electrode occurs in slightly greater concentration of permanganate than with the platinum. This is the explanation of the phenomenal fall discussed in connection with Fig. 5. There can be no decrease in voltage on passing from a reducing to an oxidizing solution but there can be, and is, a change in the relative rate of increase of the single electrode potentials. At the beginning of the titration with no ferric iron present the 2 electrodes function differently and a potential difference exists. This difference falls to zero in the presence of ferric ion. At the end-point, with zero quantity of the unreduced permanganate present, the potential difference reappears, to disappear again in the presence of permanganate ion. The end-point potential with bimetallic electrode systems is, therefore, not an oxidation potential in the same sense of the term as with electrode systems comprising a constant half-cell.

Summary

The constant half-cell of the usual electrometric titration apparatus may be replaced by a metal or certain alloys of the platinum group, other than pure platinum or pure palladium, and by tungsten. The end-point obtained with such a bimetallic system differs in character from that given by a monometallic, but is unchanged in location. The proposed electrode arrangement has the advantage of being essentially simpler than the usual system with a gain in distinctness of the end-point obtained.

This work was assisted by a grant from the Cyrus Warren Research Fund, for which the authors wish to express their thanks.

BIMETALLIC ELECTRODE SYSTEMS IN ELECTROMETRIC ANALYSIS. II. THEORY OF BIMETALLIC SYSTEMS: SYSTEMS COMPRISING TWO SIMILAR METALS

Introduction

It has been shown that the end-point in oxidimetric titrations with bimetallic electrode systems is distinguished by virtue of a difference developed in the electrodes at the end-point and which does not of necessity exist at any other time during the course of the titration. The question remains to be answered as to why there should be any potential difference developed between 2 unattackable electrodes standing side by side in the same solution.

Fredenhagen⁷ in his paper on "The Theory of Oxidation and Reduction Cells" takes up the nearest approach to a discussion of bimetallic systems. He refers the single electrode potential, unattackable-electrode-solution, to gas charges in platinized platinum by simple qualitative experiments which will be taken up later.

Two theories have been advanced for the cause of the existence of a potential between the ions of an oxidizing agent and an unattackable electrode. Le Blanc conceived of an actual interchange of charges between electrode and electrolyte as the cause of the potential difference. Nernst advanced the idea that the potential was due to an oxygen charge, in the case of a reducing agent a hydrogen charge, in the electrode. The former theory requires the conception of a charge without a corresponding ion since the metal is precluded from giving ions to the solution and likewise no deposition of metallic ions is possible. The latter explanation is entirely in agreement with the ionic theory and Faraday's law. According to this view, then, the unattackable electrode functions as a gas electrode. Fredenhagen⁷ developed the Nernst theory further.

Starting with the hypothesis that an unattackable electrode may form a solution with a gas, the expression for the single electrode potential developed, E , may be written

$$\begin{aligned} E &= E_0 + \frac{RT}{(m-n)Q} \ln \frac{(M^{m+})}{(M^{n+})} \\ &= E'_0 + \frac{RT}{2Q} \ln \frac{(H^+)^2}{(H_2)} \\ &= E''_0 + \frac{RT}{4Q} \ln \frac{(O_2)}{(O^{--})^2} \end{aligned}$$

where (M^{m+}) and (M^{n+}) represent the ion concentrations of the metal M with $m+$ and $n+$ charges; (H^+) , (O^{--}) , (H_2) the other concentrations

⁷ Fredenhagen, *Z. anorg. Chem.*, **29**, 398 (1902).

involved at equilibrium; and E_0 , E'_0 , E''_0 are the respective electrolytic potentials. The other symbols have their usual significance.

It is apparent that a definite hydrogen charge corresponds to a definite oxygen charge and the value of E increases with rising concentration of the hydrogen ion. Since the concentration of the oxygen ion falls off as the hydrogen ion increases, the ratio $(O_2)/(O^{--})^2$ must increase and with it the value of E . The potential of an oxidizing agent is thus increased by the addition of acid. In the case of a reducing agent the potential must obviously decrease under the same conditions. This explains the vast improvement of the break in strong acid solutions. The magnitude of the break depends directly on the difference in the value of E just prior to, and just succeeding, the end-point. The effect of the acid is to increase this difference.

Experimental Support of the Theory

Since the single electrode potential, unattackable-electrode solution, is determined by the solution pressure of the absorbed gases, it follows that any difference in the functioning of various unattackable electrodes must be due to a difference in their absorbing power for gas.

An electrode which has been freshly ignited and cooled in air, or which has been standing in air for some time, must be saturated with it at practically atmospheric pressure and, therefore, have a definite oxygen charge. Such an electrode if dipped into a solution of ion concentration corresponding to a lower charge must suffer a displacement of absorbed oxygen in order that equilibrium may exist with $(M^{m+})/(M^{n+})$. The concentration of the higher state of oxidation must increase but the actual displacement is extremely small. Fredenhagen calculated the possible oxidation that might be effected by a platinized platinum electrode with a surface of 7.5 sq. cm. saturated with oxygen as equal to 0.0085 cc. of 0.1 N ferrous iron. This is not only entirely negligible for any analytical purpose but is enormously in excess of any oxidation which the much smaller, bright platinum, electrodes used in electrometric work might cause. The ratio $(M^{m+})/(M^{n+})$, therefore, remains practically unchanged, and at equilibrium it is the determining factor in the value of E . This is quite clearly brought out by a determination of the electrode potentials of a number of insoluble electrodes in a solution in which the ratio $(M^{m+})/(M^{n+}) = 1$.

A solution of ferrous sulfate containing 25 cc. of 0.1 N ferrous sulfate and no ferric ion, 20% by volume of conc. sulfuric acid, was exactly $1/2$ oxidized with 0.1 N potassium permanganate solution, and the single electrode potentials of a number of unattackable electrodes were determined. The results are included in the following table.

The same measurements made with a similar solution 50% titrated with 0.1 *N* potassium dichromate also checked with the results above.

TABLE VI
SINGLE ELECTRODE POTENTIALS IN A SOLUTION CONTAINING THE SAME CONCENTRATION OF FERROUS AND FERRIC IRON

All the electrodes except tungsten were freshly ignited and cooled in air			
Electrode metal	E.m.f. Metal-AgCl Mv.	Electrode metal	E.m.f. Metal-AgCl Mv.
Pt	315	PtIr (2%)	314.5
PtRh	315	PtIr (10%)	313
W	315	PtOs(5%)	314
PtAu	316	Pd (Wire)	314.5
Ir	314.5		

Evidently the difference in the electrodes can be brought out only at the limiting ion concentration or, more comprehensively, when the system is out of equilibrium. When the concentration of either M^{m+} or M^{n+} becomes vanishingly small its osmotic pressure is no longer greatly in excess of the solution pressure of the gas in the electrode. The latter then becomes the governing factor in determining E and a difference in potential immediately develops between 2 electrodes possessing varying solvent power for gas. This potential at limiting concentration has been repeatedly pointed out in connection with ferric-ferrous and permanganate-manganous systems.

In order to demonstrate the dependence of the limiting potential upon the gas charge in the electrode, platinum, platinum-rhodium, and tungsten electrodes were submitted to various methods of pre-treatment and their potentials determined as rapidly as possible in 0.1 *N* solutions of ferrous sulfate and potassium dichromate.

TABLE VII
EFFECT OF PRE-TREATMENT ON POTENTIAL OF ELECTRODES

Electrode	Pre-treatment	E.m.f. Electrode-AgCl	
		0.1 <i>N</i> FeSO ₄ Mv.	0.1 <i>N</i> K ₂ Cr ₂ O ₇ Mv.
Pt	H ₂ Cr ₂ O ₇ (cold)	-215 to -359	+955 to +1012
		Av., -277	Av., +986
	KOH (hot)	-200 to -309	+333 to +278
		Av., -277	Av., +314
	KMnO ₄ (hot)	+203 to +288	+887 to +952
		Av., +216	Av., +921
	Ignited	-350 to -365	+357 to +480
		Av., -360	Av., +402
	SnCl ₂ + HCl (hot)	0 to -118	0 to -80
		Av., -35	Av., -46

TABLE VII (Continued)
EFFECT OF PRE-TREATMENT ON POTENTIAL OF ELECTRODES

Electrode	Pre-treatment	E.m.f. Electrode-AgCl	
		0.1 N FeSO ₄	0.1 N K ₂ Cr ₂ O ₇
		Mv.	Mv.
PtRh	H ₂ SO ₄ (33%, hot)	-9 to -357 Av., -207	+500 to +565 Av., +540
	H ₂ Cr ₂ O ₇ (cold)	-20 to -196 Av., -115	+852 to +881 Av., +863
	KOH (hot)	-300 to +100 Av., -60	+195 to +328 Av., +268
	KMnO ₄ (hot)	+200 to +218 Av., +208	+710 to +743 Av., +732
	Ignited	-330 to -358 Av., -346	+240 to +300 Av., +272
	SnCl ₂ + HCl (hot)	+30 to +90 Av., +54	-47 to +10 Av., -18
	H ₂ SO ₄ (33% hot)	-250 to +15 Av., -58	+465 to +515 Av., +497
W	H ₂ Cr ₂ O ₇ (cold)	0 to +100 Av., +50	+410 to +548 Av., +469
	KOH (hot)	-30 to -49 Av., -41	0 to +55 Av., +18
	KMnO ₄ (hot)	+300 to +325 Av., +312	+618 to +746 Av., +674
	(layer MnO ₂ on surface)		
	Polished	-43 to +16 Av., -21	-35 to +35 Av., -2
	SnCl ₂ + HCl (hot)	-117 to -177 Av., -152	-110 to -135 Av., -119
	H ₂ SO ₄ (33% hot)	-111 to -141 Av., -122	+7 to +11 Av., +9

The great variation in potential not only with different pre-treatment but with repeated applications of the same means of enforcing an unbalanced condition is at once apparent. The results at most are only qualitative. No attempt was made to make the time or manner of pre-treatment exactly uniform. In general the electrodes were merely dipped for a few seconds into the various solutions, washed, placed in the reference solution, and the potential quickly read. With cold chromic acid the treatment was extended to about 5 minutes. Platinum and platinum-rhodium were ignited to white heat and cooled in air; tungsten was polished with coarse emery cloth.

When the various methods of pre-treatment are listed in the order of increasing potential with ferrous sulfate and decreasing with potassium dichromate the results are as shown in Table VIII.

TABLE VIII
SUMMARY OF EFFECTS OF PRE-TREATMENT

Electrode	0.1 N FeSO ₄	0.1 N K ₂ Cr ₂ O ₇
Pt	Ignited	H ₂ Cr ₂ O ₇
	H ₂ Cr ₂ O ₇	KMnO ₄
	KOH	H ₂ SO ₄
	H ₂ SO ₄	Ignited
	SnCl ₂ + HCl	KOH
	KMnO ₄	SnCl ₂ + HCl
PtRh	Ignited	H ₂ Cr ₂ O ₇
	H ₂ Cr ₂ O ₇	KMnO ₄
	KOH	H ₂ SO ₄
	H ₂ SO ₄	Ignited
	SnCl ₂ + HCl	KOH
	KMnO ₄	SnCl ₂ + HCl
W	SnCl ₂ + HCl	KMnO ₄
	H ₂ SO ₄	H ₂ Cr ₂ O ₇
	KOH	KOH
	Polished	H ₂ SO ₄
	H ₂ Cr ₂ O ₇	Polished
	KMnO ₄	SnCl ₂ + HCl

The osmotic pressures of all ions concerned remain the same throughout. There was a large difference in the solution pressures of absorbed oxygen and hydrogen in the electrodes. From the mathematical expressions given it follows that the potential, unattackable-electrode-solution, is directly proportional to the solution pressure of hydrogen in an oxidizing solution and the converse in a reducing solution. In the case of both platinum and platinum-rhodium the results in general bear out this conclusion. The position of sulfuric acid is somewhat anomalous and potassium permanganate decidedly so. With tungsten it will be observed that the order reverses with stannous chloride in hydrochloric acid, chromic acid, and permanganate, indicating that the effect of the pre-treating agent was the same regardless of the reference solution. After treatment with potassium permanganate there was a very thin coat of manganese dioxide visibly adhering to the tungsten surface which was not removed by washing. A partial solution of this when the electrode is placed in the reference solution, provided migration is slow, would result in the potential $\text{MnO}_2 \rightarrow \text{Mn}^{++}$, instead of, unattackable-electrode-solution. The same effect would thus be obtained whatever the surrounding medium. The same explanation may be extended to explain the anomalous position of potassium permanganate with platinum and platinum-rhodium. Very little modification is required to extend the idea to the effect of chromic acid and stannous chloride on tungsten.

Considerable difficulty has been experienced in the past with the inactivation of platinum electrodes used in electrometric work after

repeated use in consecutive titrations, particularly with potassium dichromate. Various methods have been suggested for maintaining the electrode efficiency, such as ignition, treatment with chromic acid, ferrous sulfate, or hydrochloric acid. In order to obtain the maximum break at the end-point the condition of the electrode must be as far as possible removed from equilibrium with the solution containing excess of the titrating agent. In oxidimetric reactions, therefore, the hydrogen charge in the electrode should be as high as possible and the oxygen low. If the electrode initially has a high hydrogen charge and the titration is so quickly run that the gas charge just preceding the end-point is in equilibrium with a lower potential than the solution, the maximum possible break is obtained. The apparent beneficial effect of oxidizing agents in pre-treating must be due to a cleaning of the electrode surface whereby equilibrium is more quickly established between the electrode and the solution initially, when it is at its strongest reducing power. A rapid titration prevents continuous equilibrium and the break is decidedly better than it would have been if no pre-treatment had been resorted to.

The Effect of Continuous Polarization upon the Electrode Potential

It is evident that any quantitative comparison of the solvent power of different unattackable electrodes for gases must be made when the system is forced out of equilibrium in a more reproducible manner than by any of the pre-treatment methods so far taken up. A polarizing current was selected as the means of accomplishing this.

Suppose the simple case of an insoluble metal immersed in a solution of potassium permanganate. Equilibrium is set up between the solution and the gas charge in the electrode. If, now, this unattackable electrode is connected with a second insoluble electrode in the same solution through a source of current and subjected to an anodic polarization, a higher oxygen charge will be impressed upon it. The actual decomposition of the electrolyte is so slight with low voltage that the osmotic pressure of any ions present is not appreciably altered while the relative change in the solution pressure of the absorbed oxygen is increased considerably, thereby causing an increase in the potential, unattackable-electrode-solution. Upon the nature and degree of the solvent power of the metal for oxygen depends the magnitude of the potential alteration. With a solution of hydrochloric acid and cathodic polarization, the conditions are obviously reversed and a comparison of the effects of absorbed hydrogen is obtainable.

The single electrode potentials of tungsten-platinum and platinum-platinum-rhodium, in identical solutions, were determined. They were then submitted to the effect of a polarizing current of 0.5×10^{-5} amperes for 3 minutes. This was obtained by taking 0.5 volt from a storage bat-

tery and interposing a resistance of 100,000 ohms. A very fine platinum wire was used as a polarizing electrode. At the end of this time (the zero second) the relative change in the several potentials was read by the magnitude of the swing of the galvanometer needle on closing the circuit with the comparison electrode. The polarizing circuit was at once broken and the rate at which each electrode returned to its equilibrium potential measured.

TABLE IX
EFFECT OF POLARIZATION

A. Solution pressure of oxygen		(Anodic polarization)			
Electrolyte..	0.001 N KMnO ₄				
Polarizing current.....	0.5×10^{-5} amp.				
Period of polarization.....	3 min.				
Polarizing electrode.....	Pt wire, surface exposure, 3.8 sq. mm.				
Standard electrode.....	0.1 N KCl, AgCl, Ag.				
All readings given as measured, not reduced to absolute values.					
Electrode ^a	Surface exposure	Initial voltage	Divisions of galvanometer ^b	Deflection	Loss
	Sq. mm.	Mv.	0 Sec.	10 Sec.	%
Pt	69	+713	+32 to +60 Av., +50	+7 to +17 Av., +10	80
PtRh	49	+687	+32 to +56 Av., +46	+7 to +12 Av., +9	80
W	80	-155	-33 to -47 Av., -38	-7 to -9 Av., -8	79
(Fused) W	270	-142	-17 to -23 Av., -20	-3 to +1 Av., -2	90
(Sintered with 95% fusing current)					
B. Solution pressure of hydrogen		(Cathodic polarization)			
Electrolyte..	0.001 N HCl				
(Other conditions as under A)					
Electrode	Surface exposure	Initial voltage	Divisions of galvanometer	Deflection	Loss in 10 Sec.
	Sq. mm.	Mv.	0 Sec.	10 Sec.	%
Pt	69	+456	-17 to -29 Av., -24	-2 to -4 Av., -3	87.5
PtRh	49	+309	-7 to +8 Av., 0	-3 to +8 Av., +2	
W (Fused)	80	-82	+2 to +13 Av., +6	+2 to +13 Av., +6	0
W (Sintered)	270	-33	+8 to +14 Av., +11	+8 to +13 Av., +11	0

^a The Pt and PtRh electrodes were ignited and cooled in air before polarization. The W electrodes were polished with emery cloth.

^b A + deflection means a swing of the needle to the right, indicating an increase in voltage when E is +.

The difference in behavior of tungsten from that of the other 2 metals when polarized cathodically is interesting. There is no alteration in the displacement caused by the polarization after the current is broken. This would seem to indicate that the effect here with tungsten is not due to a solution pressure of absorbed hydrogen as such but rather to an alteration in the nature of the surface conditions due to oxidation and reduction effects.

Although the electrodes showed considerable difference on polarization it seemed advisable to investigate further the effect of current density on these differences before attempting to draw any conclusions, especially since the two forms of tungsten used possessed very different surface exposure, due to the structure of the sintered metal being much less compact than that of the fused. For this purpose the same polarization

TABLE X

EFFECT OF POLARIZATION IN SOLUTIONS CONTAINING EQUIVALENT CONCENTRATION OF ACID AND OXIDIZING AGENT

Electrode	+ Polarization		- Polarization	
	Initial voltage Mv.	Deflec.	Initial voltage Mv.	Deflec.
Electrolyte, 0.0166 <i>M</i> with respect to $K_2Cr_2O_8$, 0.1 <i>M</i> with respect to HCl				
Pt	+455	+ 41	+470	-15
PtRh	+438	+ 46	+386	- 7
W	+ 60	+ 52	+ 29	- 2
Electrolyte, 0.0166 <i>M</i> with respect to $KBrO_3$, 0.1 <i>M</i> with respect to HCl				
Pt	+653	+ 23	+495	- 9
PtRh	+520	+ 65	+315	- 3
W	-127	- 24	-141	0
Electrolyte, 0.1066 <i>M</i> with respect to KIO_3 , 0.1 <i>M</i> with respect to HCl				
Pt	+551	+ 93	+535	- 9
PtRh	+521	+109	+491	- 5
W	- 12	- 36	- 3	+ 3

Surface exposure of electrodes: Pt, 69 sq. mm.; PtRh, 49 sq. mm.; W (fused), 160 sq. mm.; Pt polarization electrode, 3.8 sq. mm.

experiments were carried out with 3 platinum wire electrodes of various surfaces but all giving the same purity test by the Bureau of Standards thermo-electric method.⁸ The current density was undeniably not without its effect and conclusions drawn from results obtained with the electrodes of Table IX are not applicable to all electrodes of these same metals without regard to size. As is to be expected the results obtained agreed only roughly. With anodic polarization, in which case the deflections are larger and show up electrode differences, increasing the current density by increasing the impressed current caused a corresponding increase in

⁸ Burgess and Sale, "A Study of the Quality of Platinum Ware," *Bur. Standards Sci. Paper*, 254 (1915).

the magnitude of the polarization, while decreasing the current density by an increase in surface exposure decreased the extent of the displacement. However, an increase in surface of 3600% fell short of cutting the polarization in half so that the effect of the different current densities involved with the electrodes dealt with here will fall within the limits of experimental error and may be omitted from the calculations.

Although the results so far show unmistakable differences in the solution pressures of hydrogen and oxygen in the several electrodes, they offer no suitable basis for the selection of the most satisfactory electrode material. In order to find an expression for this, polarization experiments similar to those given in Table IX were carried out in a solution in which the equivalent concentrations of both an acid and an oxidizing agent were equal; that is, a solution 0.1 *N* with respect to both an oxidizing agent and hydrochloric acid. The results are given in Table XI.

TABLE XI
EFFECT OF POLARIZATION ON BREAK AT END-POINT WITH MONOMETALLIC SYSTEMS

The solutions titrated contained 25.00 cc. of approximately 0.1 *N* FeSO_4 in an initial volume of 75 cc. Acidity, 33% conc. HCl . Titrating solution, 0.1 *N* $\text{K}_2\text{Cr}_2\text{O}_7$

Electrode	Polarization	0.1 <i>N</i> Soln. corresponding to break	Break
		Cc.	Mv.
Pt	None	0.04	47
	Cathodic	0.04	35
	Anodic	0.05	100
PtRh	None	0.04	26
	Cathodic	0.05	23
	Anodic	0.04	111
W	None	} No end-point	
	Cathodic		
	Anodic		

At the completion of an oxidation reaction an electrode ceases to function as a hydrogen electrode and behaves as an oxygen electrode in the presence of an excess of the oxidizing agent. It is clear from the theoretical discussion which has preceded that the magnitude of the end-point break will be determined by the solution pressure of oxygen and hydrogen dissolved in the electrode. The maximum break will be given with an electrode in which the solution pressure of hydrogen preceding, and oxygen immediately following, the end-point is the greatest possible. If the galvanometer deflections with anodic and cathodic polarization are taken as proportional to the solution pressure of oxygen and hydrogen, respectively, it will be seen at once from Table X that in every case the order of magnitude of the solution pressures in the electrodes investigated was the same, pure platinum being plainly the most desirable, and tungsten the least desirable, electrode metal.

In view of the surprising magnitude of the polarization effects, it seemed possible to utilize a low polarizing current as a continuous means of pre-treatment during the course of the titration. Cathodic polarization has the effect of increasing the apparent strength of the oxidizing agent. Either would increase the end-point break. However, in the usual solution titrated the concentration of acid, and consequently of hydrogen ion, is very high. As a result the same impressed currents would have a far greater anodic effect at the end-point, where the opposing osmotic

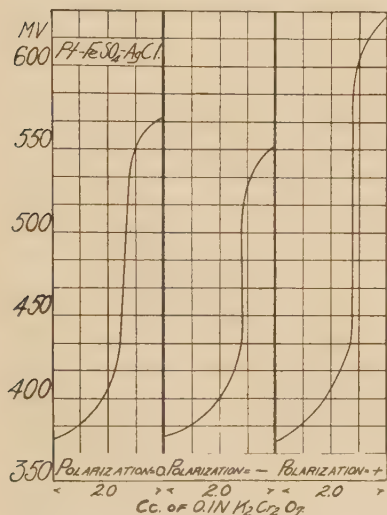


Fig. 11.

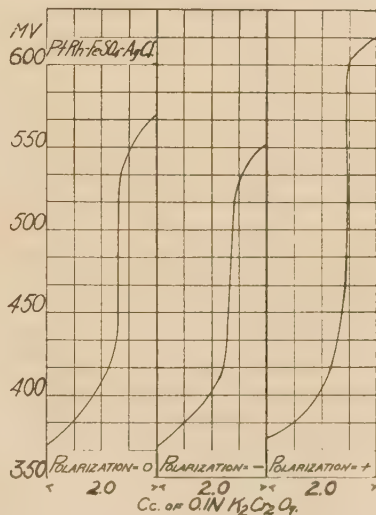


Fig. 12.

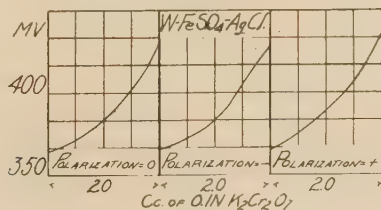


Fig. 13.

pressure of oxygen ion is very low, than cathodic effect where the osmotic pressure of hydrogen ion is always high. The disappearance of the lower state of oxidation in such high acid concentration causes no appreciable alteration in the osmotic pressure of hydrogen ion.

In order to demonstrate this conclusion titrations were run with each of the 3 electrodes previously used with a silver chloride half-cell. First the metallic electrodes were unpolarized, then cathodically, and, finally, anodically polarized. A very small platinum electrode formed

the other pole of the polarizing circuit. The current was 0.5×10^{-5} amperes and was applied during the entire course of the titration. The results are tabulated on page 26.

Figs. 11, 12, and 13 show graphically the conditions given in Table XI.

Not only is there no increase in the magnitude of the break with negatively polarized platinum and platinum-rhodium electrodes, but there is an actual lessening, due to the apparent weakening of the oxidizing agent. There is no doubt but that positive polarization effects a very material improvement in the break.

With bimetallic combinations of the preceding electrodes, polarization gave even more marked results.

TABLE XII

EFFECT OF POLARIZATION ON BIMETALLIC SYSTEMS WITH DISSIMILAR METALS

The solutions titrated contained 25.00 cc. of approximately 0.1 *N* FeSO_4 in an initial volume of 75 cc. Acidity, 33% by volume of conc. HCl . Titrating solution, 0.1 *N* $\text{K}_2\text{Cr}_2\text{O}_7$.

Electrode system	Polarization ^a	0.1 <i>N</i> Soln. corresponding to break	Average break
		Cc.	Mv.
Pt-PtRh	None	0.05	36
	Cathodic	0.05	34
	Anodic	0.05	98
Pt-W	None	0.06	52
	Cathodic	0.05	29
	Anodic	0.06	120

^a Referred to platinum.

In these last experiments no third electrode was used for the polarizing circuit. One of the metallic electrodes was made the positive pole and the other the negative. The results are shown graphically in Figs. 14 and 15.

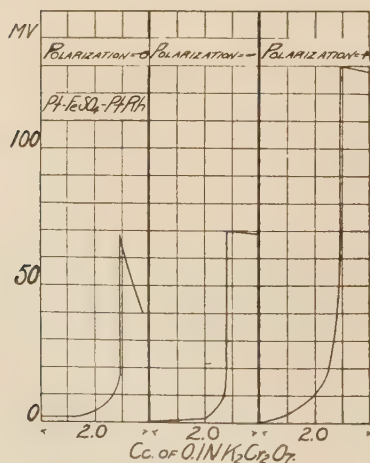


Fig. 14.

Theoretically, at least, since the effect of polarization upon the break with a single metallic electrode depends upon the normal magnitude of that break, the best possible end-point with a polarized bimetallic system should be obtained with both electrodes of the same metal, and that metal should be the one that normally shows the greatest change as the titration passes through the end-point. Table X showed platinum to be this metal.

Two platinum electrodes were dipped into a solution of ferrous sulfate so that equal areas were exposed, the usual polarizing current was applied, and the solution titrated with 0.1 *N* potassium dichromate. When No. 1 was the anode the break at the end-point was about 190 mv., but when it was the cathode the break dropped below 90 mv. Apparently, this is a much more sensitive test of the relative purity of platinum than the thermo-electric method, for the wires showed no difference in the latter test. With unpolarized wires the system became extremely sluggish in the region of the end-point but gave a discernible break of about 20 mv.

To insure the absolutely identical character of the electrodes No. 1 was cut in two and used for both poles. No end-point was now obtained with unpolarized electrodes, but when polarized the end-point was the sharpest ever obtained with any system and was not affected by a reversal of the impressed current.

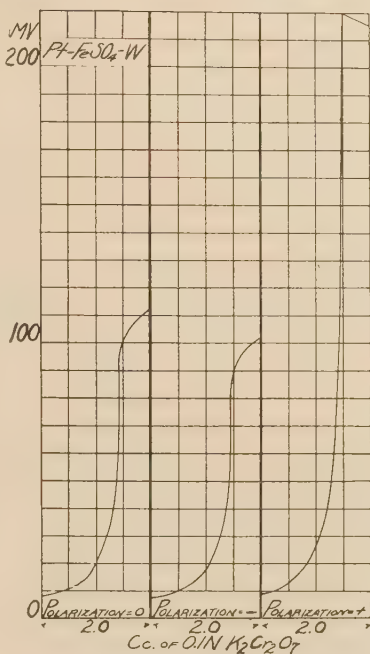


Fig. 15.

TABLE XIII

EFFECT OF POLARIZATION ON BIMETALLIC SYSTEMS WITH SIMILAR METALS

The solution titrated contained 25.00 cc. of approximately 0.1 *N* FeSO_4 in an initial volume of 75 cc. Acidity, 33% HCl . Titrating solution, 0.1 *N* $\text{K}_2\text{Cr}_2\text{O}_7$

Electrode system	Polarization	Initial voltage ^a		Av. break Mv.
		Polar. Cur. 0 Mv.	Polar. Curr. 0.5×10^{-6} amps. Mv.	
1-2	None			21 (Sluggish)
	1+	4	42	180
	1-	1	42	88
1-1	None	No end-point, sluggish in that region.		
	Right + ^b	0.5	35	216
	Right -	0.5	29	196
W-W (fused)	Right +	No end-point		
	Right -	No end-point		

^a The initial voltages due to polarization fell very rapidly, as always with bimetallic systems, upon the addition of the oxidizing agent.

^b The right-hand electrode was made the anode.

Summary

There seems to be no further evidence necessary to prove that with aqueous solutions of multivalent elements in which the concentration of one state of oxidation approaches either limiting value, the potential, unattackable-electrode-solution, is determined by the magnitude of the solution pressure of gas absorbed by the electrode, and the end-point obtained in oxidimetric titrations with systems comprising 2 unattackable electrodes is given only by virtue of a difference in the solvent power of the 2 metals for gas. When the concentration of oxygen ion, or hydrogen ion, becomes vanishingly small, the osmotic pressure is too low for an immediate saturation of the electrodes with the corresponding gas. A difference in potential develops which is at its maximum with minimum concentration of the corresponding ion and which falls rapidly as this ion concentration rises to a value in excess of that required for the saturation of both electrodes.

The proposed bimetallic system⁹ provides a type of electrode system essentially different from those previously adopted.¹⁰ A comparison of the relative values of the regular monometallic and bimetallic systems may be based upon the difference in the mechanics of the end-point in the two cases. The change in voltage with the former, which is a true oxidation potential, is continuous throughout and rises to a maximum at the end-point. With the latter practically all change is confined to within less than 0.5 cc. of the completion of the titration. Although the actual magnitude of the break is normally less than with monometallic combinations, it is, relative to the preceding rise, much greater, hence the sharpness of the end-point is correspondingly increased, insuring greater speed and accuracy. With the use of polarized bimetallic systems the break may be increased so much as to leave no possible comparison favorable to the monometallic system. It is thus possible to titrate solutions which offer too small potential differences between two possible states of oxidation for a good end-point with the regular apparatus.

The polarizing circuit may be made so integral a part of the usual

⁹ This is not the first system to make use of polarization effects. Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911), used a polarized platinum electrode with the regular system, [p. 5 (I)] for a number of precipitation reactions. A second platinum electrode formed the other pole of the polarizing circuit and the applied e.m.f. was greater than that used in the work described here. A calculable amount of the metal under investigation was deposited upon the electrode during the course of the titration. The results obtained were not, on the whole, satisfactory.

Merriam, "The Theory of the Residual Current," (*Dissertation*, Göttingen, 1906), used a polarized system for neutralization reactions. A stream of hydrogen was conducted through the solution during the titration.

¹⁰ This thesis, page 7.

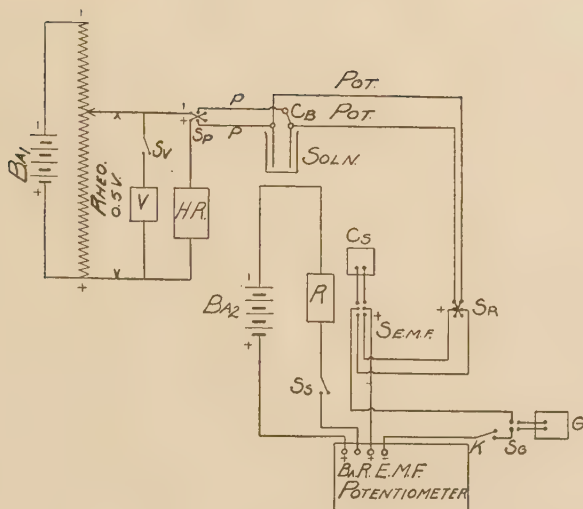


Fig. 16

Key to Fig. 16

Ba ₁ , Storage battery for polarizing.	POT.-POT., Leads from electrodes to potentiometer system.
Ba ₂ , Edison storage battery.	Soln., Beaker containing solution to be titrated.
RHEO., Rheostat for taking off polarizing voltage. About 0.5 volt used.	S _r , Reversing switch.
V, Voltmeter.	S _{e.m.f.} , Switch for throwing in standard cell or solution to be titrated.
Sv, Voltmeter switch.	C _s , Standard cell.
H.R., High resistance, 100,000 ohms.	R, Setting resistance for potentiometer.
Sp, Reversing switch for polarizing circuit.	S _s , Battery switch.
P,P, Polarizing leads to electrodes.	S _g , Galvanometer switch.
C, Mercury cup commutator.	G, Galvanometer.
B, Removable bridge in case monometallic systems is desired.	K, Tapping key.

The potentiometer was a "students'" potentiometer. This instrument was found satisfactory for all purposes. It may be operated rapidly and its accuracy is entirely sufficient. The galvanometer was the ordinary lamp-and-scale box-type. A potential difference of 1 mv. through the potentiometer circuit caused a deflection of 10 scale divisions.

On account of the convenience of its buret and beaker supports, a Kelley electro-metric titration apparatus was partially remodeled for use here. The electrode connections were removed, since no use was made of the potentiometer system, and the entire calomel electrode arrangement discarded. A small 3-cup mercury commutator, C in the diagram, was mounted on the reservoir support. By removing the wire bridge, B, the polarizing circuit was broken and only the regular potentiometer system remained.

The polarizing circuit is self-explanatory. There is no necessity that the high resistance interposed be accurate. A carbon resistance answers the purpose very well.

The particular electrode combination used in any case is described in the discussion of the given titration. For most of the work two identical platinum electrodes were used. In the early part of the investigation a special platinum was used almost entirely but later "C.P." platinum thermocouple wire was obtained in several sizes which was perfectly satisfactory. Usually, the wires were securely attached to short pieces of B. and S. No. 8 copper wire by winding tightly with fine copper wire, slipped through small rubber stoppers, and inserted in the electrode supports of the Kelley apparatus. The heavy copper wire provided a firm support for screw connections and saved wear and tear on the fragile platinum. When it was found necessary to use short pieces of wire they were sealed into Pyrex tubing and connections made with the lead wires by filling the tubes with mercury.

apparatus that it requires no attention and presents no difficulties.¹¹ Uniform results are insured, there is no possible inactivation of the electrodes, no stopping for electrode pre-treatment of any kind, none of the inherent bother of the standard half-cell.

As for the disadvantages of the new system, the greater localization of the total potential change makes it more difficult to anticipate the end-point as readily as with the other apparatus. Enough warning is given, however, to make the danger of over-titration negligible after a very little practice. Obviously, from the equations for the electrode potential, the velocity of the titration reaction must be infinitely great in comparison with the velocity of the back diffusion of the absorbed gas in the 2 metal electrodes. This prerequisite makes the question of reaction velocities of greater importance than with the monometallic system and renders the latter more desirable for certain titrations.

¹¹ The apparatus used in all work described here is shown diagrammatically in Fig. 16.

PART II.

APPLICATIONS.

A NEW METHOD FOR THE ELECTROMETRIC TITRATION OF VANADIUM IN THE PRESENCE OF IRON AND CHROMIUM

Introduction

Of the two accepted methods for the selective oxidation of vanadium in the presence of chromium, titration with potassium permanganate and boiling with nitric acid, neither is free from inaccuracies due to manipulation. The end-point in the former, especially in the presence of relatively large amounts of chromium, is extremely difficult to detect,¹² and the latter requires an extended period of boiling with a high and regulated concentration of nitric acid.¹³ It seemed desirable, therefore, to investigate further the selective reactions of these 2 elements with a view to simplifying the analytical procedures now in wide use.

Gooch¹⁴ calls attention to a method worked out by H. E. Palmer for the separation of chromium and vanadium which is based upon the reduction of chromate by hydrogen peroxide in acetic acid solution, leaving unchanged the vanadate which may then be precipitated directly by the addition of lead acetate. As it stands, the method is of little more than theoretical interest but it offers possibilities as the basis of a volumetric method for vanadium involving an electrometric titration of the vanadate with ferrous sulfate. When the concentration of hydrogen ion is low, hydrogen peroxide readily oxidizes a chromic salt to chromic acid; as it rises, the amount of oxidation decreases until finally the peroxide reduces chromic acid to a chromic salt. Perchromic acid is often an intermediate product in this reduction. The presence of chromium and iron also influences the action of hydrogen peroxide on vanadic acid, and it was necessary, therefore, to make a careful study of this reaction before it could be applied to the determination of vanadium in the presence of these other elements.

Character of the Titration

First, it is advisable to discuss the electrometric titration of vanadic acid with ferrous sulfate. The electrode system used was the polarized bimetallic system previously described, consisting of 2 identical platinum wires polarized with a current of 0.5×10^{-5} amp. (0.5 volt through 100,000 ohms). Preliminary titrations made on solutions containing vanadic acid alone, and also in the presence of chromium and chromium and iron, with various mixtures of mineral and acetic acids, showed that the end-point was sharp and much less affected by the concentration of hydrogen

¹² Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 722 (1916).

¹³ Kelley, Wiley, Bohn and Wright, *ibid.*, **11**, 632 (1919).

¹⁴ Gooch, "Methods in Chemical Analysis," J. Wiley and Sons, 1912, p. 412.

ion and the presence of foreign salts than that given by a monometallic system. The initial voltage of a solution containing vanadic acid lies considerably above that of a solution of chromic acid of equivalent normality and the same concentration of hydrogen ion, as is to be expected from a consideration of the relative oxidizing strengths of the two acids and the concentration of oxygen ion given by each. An increase in acidity lowers the potential of either oxidizing agent, thereby increasing its apparent strength.

Taking into consideration the inherent characteristics of the two systems, the titration of vanadic acid with ferrous sulfate, using the bimetallic system, is perfectly analogous to that with the monometallic.¹⁵ The voltage rises slowly from the first addition of reducing agent, more slowly as the concentration of vanadyl salt increases. Just preceding the end-point, this velocity increases very slightly, then decreases again to an almost imperceptible rise. At the end-point the galvanometer appears to have momentarily lost its sensitivity and then reverses the direction of its swing as more ferrous sulfate is added. In carrying out a titration it is best to follow the rising voltage with the potentiometer, keeping about 0.5 mv. behind it. With so sensitive an electrode system this is quite sufficient to give an easily determined swing of the galvanometer. Ferrous sulfate is added more and more slowly as the rate of the potential rise decreases until the deflection indicates a diminishing potential. The end-point lies just beyond the brief period of insensitivity. An excess of the reducing agent causes the voltage to decrease with rapidly increasing velocity until the approximate limiting concentration is passed and the stable condition reached. The reversal is very sharp, easy to detect, and normally sensitive to 0.03 cc. of 0.02 *N* solution. The total magnitude of the preliminary rise varies considerably with the composition of the solution. With a pure, strongly acid solution of ammonium vanadate it may amount to from 200 to 300 mv., while in the determination of vanadium in a low-vanadium steel 10 to 20 mv. is common. The initial potential also alters with the concentration of acid and foreign salts. It usually lies between 350 and 500 mv. with a polarizing potential of 0.5 volt. The sharpness of the end-point, however, is hardly affected by these factors. It is advisable to keep the concentration of mineral acid fairly high, but it may vary within wide limits without causing any material difference in behavior.

Experimental

Since most of the analytical work on vanadium is devoted to special steels and similar alloys, experimental conditions were chosen closely resembling a sulfuric acid solution of an alloy steel.

¹⁵ Kelley and Conant, *J. Am. Chem. Soc.*, **39**, 341 (1916).

The iron was taken in the form of a solution of ferrous sulfate. To this was added 4.0 cc. of conc. sulfuric acid, then the chromium as potassium dichromate and the vanadium in the form of a solution of pure ammonium vanadate, standardized by titration electrometrically with ferrous sulfate which had been compared with a standard solution of potassium dichromate. A slight excess of a concentrated solution of potassium permanganate was run in; a known amount of sodium acetate and acetic acid added, then the reducing agent, either the ordinary 3% solution of hydrogen peroxide or a solution of sodium perborate neutralized with acid. After the solutions had been boiled to destroy the excess of the peroxide they were cooled to at least 20–25°, and 25–50 cc. of conc. hydrochloric acid was added before titration. The standard ferrous sulfate solution was compared with a standard 0.05 *N* vanadate solution by diluting 25.00 cc. of the latter to about 40 cc., acidifying with 15–20 cc. of conc. hydrochloric acid and titrating electrometrically.

As chromium is but slightly oxidized by hydrogen peroxide in weak acid solution, it seemed possible that the method might be made one of selective oxidation by leaving the vanadium all in the vanadyl form, oxidizing the iron with nitric acid and depending upon the peroxide for a complete conversion to vanadic acid. This attempt to eliminate the permanganate oxidation was unsuccessful.

Nitric or hydrochloric acid solution may be substituted for the sulfuric acid without affecting the results.

The period of boiling necessary to destroy completely all excess of the peroxide was one of the first points of importance to be determined. Samples were made up as outlined containing 1 g. of iron, 64 mg. of chromium, 31.9 mg. of vanadium, 4.0 cc. of conc. sulfuric acid; 20 cc. of glacial acetic acid; 20 g. of sodium acetate trihydrate, and 0.7 g. of sodium perborate in an initial volume of 200 cc. After boiling for periods of 5, 10, 15, and 40 minutes, the amounts of vanadium found were 32.4 mg., 32.4 mg., 31.83 mg., and 31.87 mg., respectively. As 15 minutes was sufficient and 40 minutes not excessive, 20 minutes was adopted as the standard period. Very long boiling causes a slight reduction of vanadic acid.

When a solution of hydrogen peroxide was used instead of perborate, vanadic acid was very appreciably reduced if the time of boiling was prolonged or considerable peroxide was added. This was probably due to a preservative in the hydrogen peroxide. As a solution of sodium perborate neutralized with acid was free from this objection it was regularly used.

When insufficient acid is present the chromic acid is not completely reduced; this error increases rapidly with the concentration of chromium. Both these factors must, therefore, be controlled. The upper limit of acidity is that at which pervanadic acid is formed, inasmuch as this decomposes on boiling to form some vanadyl salt. This limit was found to be equivalent to 0.075 *N* sulfuric acid. However, an attempt to decrease the amount of acetate added so as to leave a calculated amount of free

sulfuric acid was unsuccessful. Iron precipitated, carrying with it much of the chromate. A high concentration of free acetic acid is necessary for quantitative results.

Effect of Varying the Concentration of Acetic Acid and Sodium Acetate

The effect of the concentration of acetic acid upon the accuracy of the vanadium determination, both in the presence and absence of chromium and iron, is taken up in Table XIV.

TABLE XIV
EFFECT OF THE CONCENTRATION OF ACETIC ACID¹⁶

The solutions titrated contained 31.9 mg. of V, the stated amount of Cr, Fe, and glacial acetic acid, 4.0 cc. of H_2SO_4 (sp. gr. 1.83) 20 g. of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, and 0.7 — 2.5 g. of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$; they were boiled for 20 min. The standard FeSO_4 solution was 0.02 *N*.

Cr Mg.	Fe G.	CH_3COOH % by vol.	Initial vol. Cc.	Error Mg. V
0	0	0	200	0.0
32	1	0	200	-0.08
320	1	0	400	Fe pptd. on boiling. Con- siderable H_2CrO_4 present.
32	0	5	200	+0.05
32	0	10	200	+0.3
160	0	10	200	0.0
320	0	10	200	+1.0
320	1	16	400	+0.10
320	1	19	400	+0.10
320	1	25	200	+2.0
320	1	25	400	-0.04
320	1	33	225	-0.25

The presence of iron is distinctly beneficial, and with large amounts of chromium the error may be reduced by dilution. The last 5 experiments show that in the presence of iron with proper regulation of acidity and volume the interference of chromic acid may be prevented.

The results in the last two experiments in Table XIV are a little low, indicating a possible reduction of vanadic acid. To test this point ammonium vanadate alone, acidified with sulfuric acid and treated with acetic acid and acetate, was titrated. In high concentrations of acetic acid the reduction of vanadic acid was appreciable but between 20 and 30% the error was negligible.

Later work on steels indicated that with 1 g. of iron its catalytic effect had not quite reached its finite value. With still larger amounts the limits are extended somewhat but it is safe to state as a general rule that in the presence of at least 1 g. of iron the reaction is selective and independent

¹⁶ The results stated in Tables XIV and XV are, in each case, the averages of several determinations.

of the vanadium present if the concentration of the acetic acid added is from 20 to 25%. The initial volume should be 200 cc. when the chromium is not more than 150 mg., and 400 cc. when it rises as high as 300 mg.

In view of the enormous repression of the dissociation of acetic acid by sodium acetate it seemed possible that any excess of the latter over that required for combination with the mineral acid might have a very appreciable tendency toward lowering the effective acetic acid concentration. Throughout the work so far some excess of acetate has been present; 4.0 cc. of conc. sulfuric acid was regularly added to the ferrous sulfate used in making up the samples. This is the equivalent of 19.4 g. of sodium acetate trihydrate. In the oxidation process with permanganate part of this acid is used up. This consumption amounts to 0.5 cc. per g. of iron, or the equivalent of 2.4 g. of acetate. No account was taken of this; therefore, with all samples containing iron, excess acetate was present. It seemed desirable to extend the investigation.

TABLE XV
EFFECT OF THE CONCENTRATION OF ACETATE

The samples contained 31.9 mg. of V, 1 g. of Fe, the stated amount of Cr and excess of sodium acetate, 4.0 cc. of H_2SO_4 (sp. gr. 1.83) 20% glacial acetic acid, and 0.7 g. of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$. The initial volume was 200 cc. The actual weight of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ added in each case was 19.4 g. plus the given excess.

Cr Mg.	Excess $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ G.	Error Mg. V
32	2.5	0.0
32	12	-0.3
100	2.5	-0.09
100	12	+0.08
100	17	+0.07
100	22	Large quantities of Fe pptd. on boiling. No titration.
160	2.5	-0.09
160	12	+0.2

Considerable excess of sodium acetate has no deleterious effect upon the titration. Apparently with at least moderate amounts of chromium, provided the acetic acid content is fairly high, the limiting concentration of acetate is that at which considerable iron is precipitated on boiling. Increasing the amount of iron to 5 g. has only a slight effect on the results in Tables XIV and XV.

Determination of Vanadium in Artificial Mixtures and in Steels

Before testing the method on actual steels, samples were made up for titration corresponding to a 5g. sample of a steel containing 0.204% of vanadium and 4.0% of chromium. This was done essentially as outlined above. Ammonium vanadate and potassium dichromate were added to

a solution of ferrous sulfate containing sulfuric acid, the mixture was heated to boiling and most of the iron oxidized with nitric acid. The oxidation was completed with a slight excess of potassium permanganate, the calculated amount of sodium acetate to combine with the sulfuric acid added, then the acetic acid and neutralized solution of perborate in the amount stated in Table XIV.

In Samples 1 and 2, where the negative error was large, there was present a considerable quantity of a light yellow, crystalline precipitate which did not go into solution when the hydrochloric acid was added just before titrating. In Samples 3 to 8 the amount of the precipitate was much smaller and the results were better. Reducing the iron content in Expts. 9 to 12 by the use of smaller samples eliminated this precipitate alto-

TABLE XVI

DETERMINATION OF VANADIUM IN SYNTHETIC STEELS

All solutions contained 10.2 mg. of V, 200 mg. of Cr, 4.0 cc. of H_2SO_4 (sp. gr. 1.83), 20 g. of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, and Fe, glacial acetic acid and $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ in the amounts stated.

Expt.	Fe G.	CH_3COOH %	$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ G.	Initial vol. Cc.	Error Mg. V
1	4.75	15	2.0	400	-0.85
2	4.75	15	2.0	400	-0.70
3	4.75	10	1.5	200	-0.25
4	4.75	20	1.5	200	-0.11
5	4.75	20	0.7	200	-0.01
6	4.75	20	0.7	200	-0.11
7	4.75	20	0.7	300	-0.14
8	4.75	20	0.7	400	+0.02
9	3	20	0.7	200	+0.02
10	3	20	0.7	200	+0.02
11	3	20	0.7	300	+0.19
12	3	20	0.7	400	+0.12

gether. It seldom appeared even with 5 g. of *steel*. It contained no vanadium but its composition was not further investigated. The presence of the finely divided solid seems to cause low results,¹⁷ and any precipitate should be filtered off to avoid this error.

Two samples of vanadium steel from the U. S. Bureau of Standards were now analyzed according to the above procedure, using 5g. samples of No. 30a and 4 g. of No. 24. For the sake of completeness, the chromium was determined in No. 30a by persulfate oxidation and electrometric titration as given by Kelley and others¹⁴ but using the bimetallic electrode system. The end-point is the previously described vanadium end-point.

The effect of tungstic acid on the determination of vanadium was investigated, using 2 steels containing tungsten, chromium, and vanadium. An exact analysis of the steels was not available but it was known that

¹⁷ This Thesis, p. 42.

Steel a was approximately 2.8% of chromium, 1.3% of vanadium and 16.8% of tungsten, and Steel b, 5.2% of chromium, 0.3% of vanadium and 10.0% of tungsten. The process of solution was somewhat different from that followed by Kelley and others.² One-g. samples of a and 4 g. of b were treated with hydrochloric acid, sp. gr. 1.13, until action ceased, then 8 cc. of conc. nitric acid was added and the solution evaporated to 20 cc. After the liquid was diluted with hot water and heated until the soluble salts were dissolved, the procedure was exactly as usual. The results of the analysis were erratic and all low. Other samples were dissolved and the tungstic acid filtered out after the evaporation and solution of the salts. Under these conditions no difficulties were encountered.

TABLE XVII
DETERMINATION OF VANADIUM IN CHROMIUM-VANADIUM
Steels from the Bureau of Standards

Sample	V found %	B. of S. certificate value %	Cr found %	B. of S. certificate value %
30a	0.201			
	0.200			
	0.205		1.037	
	0.201		1.042	
	Av. 0.202	0.21	Av. 1.04	1.02
24	0.139			
	0.139			
	Av. 0.139	0.15 ^a		

^a B. of S. results, 0.143% of V.

The filtered and washed precipitates of tungstic acid were dissolved in sodium carbonate, oxidized with hydrogen peroxide, the excess of which was destroyed by boiling, and then acidified with 3 to 5 cc. of conc. phosphoric acid. After adding the equivalent of 3 to 5 cc. of conc. sulfuric acid, the occluded vanadium was titrated with ferrous sulfate. The results are stated in Table XVIII.

TABLE XVIII
DETERMINATION OF VANADIUM IN CHROMIUM-VANADIUM-TUNGSTEN STEELS

Steel	Uncorrected % V	Occluded % V	Corrected % V	% W	V occluded per % W
a	1.319	0.016			
	1.321	0.013			
	Av. 1.320	Av. 0.015	1.335	16.8	0.0009
b	0.281	...			
	0.278	0.033			
	0.282	0.028			
	Av. 0.280	Av. 0.031	0.31	19.0	0.0017

The correction for Steel a corresponds very closely to that given by Kelley,² 0.001% for each per cent. of tungsten, but in the second case it is much higher. The sample used was, however, twice as large as specified by him.

The occluded vanadium did not account for the error encountered when the tungstic acid was not removed. In view of former difficulties it was concluded that the presence of any finely divided precipitate causes the reduction of vanadic acid in this reaction.

Synthetic molybdenum-chromium-vanadium steels were analyzed for their vanadium content. Under the conditions of the titration the reduction of molybdic acid by ferrous sulfate is so slow as to render the reaction selective. There is no appreciable alteration in the end-point.

Recommended Procedure

The recommended procedure for the determination of vanadium in special alloy steels is as follows.

a. For Vanadium and Chromium-vanadium Steels.—A sample requiring about 10 cc. of 0.02 *N* ferrous sulfate is convenient. Place it in a 600cc. beaker, add 20 to 30 cc. of water and run in a measured volume of conc. sulfuric acid from a buret. Each gram of steel requires 1.0 cc. of the acid to form ferrous sulfate and a 4cc. excess is sufficient to effect a rapid solution. Heat gently until the sample is completely dissolved and the salts begin to separate. Dilute with 20 cc. of hot water and heat until dissolved. Add 4 or 5 cc. of conc. nitric acid cautiously and boil. Complete the oxidation of iron and vanadium with a slight excess of a solution of potassium permanganate. Add sufficient sodium acetate (a moderate excess does no harm), to combine with the acid used in excess of that required for solution (1 cc. of conc. sulfuric acid, = 4.8 g. of sodium acetate trihydrate), and 40 to 50 cc. of glacial acetic acid. Add about 0.5 g. of sodium perborate, previously neutralized; dilute, if necessary, to 200 cc. and boil for 20 min. Cool to room temperature, add 25 to 30 cc. of conc. hydrochloric acid and titrate with 0.02 *N* ferrous sulfate solution standardized against potassium dichromate.

b. For Chromium-vanadium-tungsten Steels.—Treat the samples with 40 cc. of hydrochloric acid, 3 parts of conc. acid to 1 of water, and heat until action ceases. Add 8 to 10 cc. of conc. nitric acid, dropwise, until the first violent action has ceased. Boil and evaporate to about 20 cc. Dilute with hot water and heat to insure complete solution of soluble salts. Filter and wash with hot 2% hydrochloric acid. Oxidize the filtrate with permanganate solution and add sufficient sodium acetate to combine with the free acid. This may be estimated accurately enough by putting the weight of hydrochloric acid as equal to 20% of the volume after concentrating the solution to about 20 cc. and adding 5 or 6 g. more

as a safeguard; 1 g. hydrochloric acid = 3.73 g. of sodium acetate trihydrate. From here the determination is carried on as outlined above.

To determine the vanadium occluded by the tungstic acid, dissolve the latter in sodium carbonate. Add a few tenths of a gram of perborate and boil vigorously for 10 minutes. Acidify with 3 to 5 cc. of phosphoric acid, add 25 to 40 cc. of sulfuric acid, 1 part of acid to 3 of water, and titrate with ferrous sulfate electrometrically to the permanent drop in potential.

c. For Molybdenum-chromium-vanadium Steels.—Exactly as in (a).

The Electrometric Titration of Small Amounts of Vanadium in Tungstic and Molybdic Acids

Samples of pure tungstic acid were dissolved in sodium carbonate solution, and acidified with phosphoric acid; dil. sulfuric acid and a known amount of ammonium vanadate were added and the mixture was titrated with ferrous sulfate. The character of the vanadium end-point is quite materially altered by the presence of the phosphotungstic acid. As the titration progresses the solution becomes a deep amethyst color, believed to be due to the formation of a vanadyl phosphotungstate, and some distance from the end-point each drop of ferrous sulfate causes a fall in potential followed by a slow return to the former maximum. The period of depression increases slowly to longer than a minute. The first decrease in voltage lasting 2 minutes or longer may be assumed to be permanent and accepted as the true end-point.

TABLE-XIX
DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN TUNGSTIC ACID

WO ₃ taken G.	% V in sample	V taken Mg.	Error Mg. V
10	0.10	10.20	+0.06
5	0.20	10.20	0.00
2	0.50	10.20	-0.03

In spite of the disadvantage of the slow end-point the results are perfectly satisfactory.

Similar samples of pure molybdic acid were dissolved in sodium carbonate solution, acidified with phosphoric and hydrochloric acids, ammonium vanadate was added and the mixtures were titrated. When sulfuric acid alone is used the end-point is slow but the use of hydrochloric acid overcomes this difficulty and the method is rapid and accurate.

It may be pointed out that the method outlined here may be applied to the direct titration of the vanadium occluded by the phosphomolybdate precipitate.¹⁸

¹⁸ Cain and Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912). *J. Am. Chem. Soc.*, **43**, 2552 (1921).

Summary

1. A polarized, bimetallic electrode system affords a more sensitive means of determining the end-point in the reduction of vanadic acid by ferrous sulfate than the usual monometallic combination.

2. In acetic acid solution the reduction of chromic acid by hydrogen peroxide in the presence of vanadic acid may be made selective and gives an excellent means of determining the latter element in all alloy steels. Results checking to 0.005% when using 5g. samples are readily obtained. One advantage over the method involving selective oxidation of vanadium with nitric acid lies in the shortened period of required boiling.

3. Traces of vanadium may be titrated directly in the presence of large quantities of phosphotungstate and phosphomolybdate. **1**

THE BIMETALLIC ELECTRODE SYSTEM APPLIED TO NEUTRALIZATION REACTIONS

—In the introductory part of the work on bimetallic electrode systems the expressions for the potential of an unattackable electrode dipping into an oxidizing solution were given.¹⁹ It was pointed out at that time that the end-point in case of oxidimetric titrations carried out electrometrically with two metallic electrodes depended upon a differential solution pressure of absorbed gas becoming effective at the limiting ionic concentrations. From an inspection of the equations there seemed to be no reason why, if a neutral solution of an oxidizing agent were added to an acid solution of unknown strength, the bimetallic system should not serve as an indicator in the neutralization of the latter. A potential difference existing prior to the end-point should tend to disappear as the solution reaches exact neutrality, or the break should be downward. If the end-point were approached from the opposite direction, that is, alkaline to acid, the break should be upward. In brief, the end-point phenomenon of a neutralization reaction should be perfectly reversible.

A 0.1 *N* solution of hydrochloric acid was prepared and portions of it titrated with an approximately equivalent sodium hydroxide solution under various conditions. The usual electrometric arrangement was used, namely, 2 platinum wire electrodes with a polarizing voltage of 0.5 volt through an external resistance of 100,000 ohms. When the sample titrated contained only a dilute solution of hydrochloric acid the galvanometer was extremely sluggish in the region of the neutral point. An apparently enormous resistance was set up within the solution, the measuring instruments lost their sensitivity and no end-point was obtainable. The addition of potassium bromate did not improve matters. When, however, a neutral solution of hydrogen peroxide²⁰ was added the normal sensitivity continued throughout; a potential difference persisted to within 0.3 to 0.4 cc. of 0.1 *N* titrating solution of the end-point, then began slowly to decrease and at the neutral point a clear, sharp, downward break occurred. With the reversed titration a rise preceded the end-point which was marked by an upward break of about 100 mv. A slight excess of acid caused the voltage to fall. In both cases the point of maximum velocity of potential change was exactly coincident with the "green point" of bromothymol-sulfonephthalein which corresponds to a P_H value of 6.8. In neither case was the end-point permanent. The rapid stirring of the

¹⁹ This Thesis, page 20.

²⁰ The hydrogen peroxide used was the ordinary 3% commercial solution; 100 cc. was neutralized with sodium hydroxide, using bromothymol-sulfonephthalein as the indicator, and diluted to 250 cc.; 5 cc. of this solution was added to each sample titrated.

A solution of hydrogen peroxide prepared by neutralizing sodium perborate with hydrochloric acid failed to give satisfactory results.

solution favored the absorption of carbon dioxide to such an extent that variable results were obtained in consecutive titrations approaching the neutral point from the alkaline side. With the approach on the opposite side the crawl as the end-point was passed was not sufficient to impair seriously the clarity of the break.

The method seems to offer very favorable possibilities for an extensive development of a new type of hydrogen electrode that is unique in its independence of an external gas supply. In view of further work along this line, the publication of which must be delayed, it is desired to call brief attention at this time to this application.

THE ELECTROMETRIC TITRATION OF SELENIUM IN THE PRESENCE OF TELLURIUM, IRON AND COPPER

Introduction

The reduction of selenious acid to metal by titanous chloride was observed by Moser²¹ and also by Monnier.²² Moser attempted to develop a volumetric method for selenium based on this reaction using methylene blue as indicator but the results obtained were invariably too high. This was due to the further reduction of the selenium to hydrogen selenide, a compound which had been shown to exist under similar conditions by Pleischl²³ and Trautmann.²⁴

Under the condition imposed by Moser, namely, a hot hydrochloric acid solution, the electrometric end-point is either absent or very poor, but in a cold solution containing 25 to 75% of conc. hydrochloric acid and saturated, or nearly so, with sodium chloride, the end-point with the previously described polarized bimetallic electrode system with platinum electrodes is excellent. The presence of the sodium chloride is important. It insures rapid and uniform coagulation of the selenium hydrosol and increases the sharpness of the change in voltage at the end-point. The use of a cold solution also eliminates the almost inevitable loss of selenium by volatilization.

The character of the end-point for this titration is somewhat difficult to describe but is readily discovered by experiment. After enough of the titrating solution has been added to give a constant potential, there is little change until within a short distance of the end-point. Slight fluctuations in the e.m.f. may be manifested; the resistance of the solution is so low that the galvanometer is extremely sensitive. The characteristic rise occurs, with the fall immediately following. The condition of the solution with respect to acidity and foreign salts determines which of the two predominates. Increasing the polarizing e.m.f. from 0.1 to 1.0 volt makes no appreciable difference in the character of the end-point.

As is the case with other titanous titrations the actual voltage change may not be large, in fact may not amount to more than a few millivolts. The galvanometer should be sufficiently sensitive to give a distinct deflection for a change in potential of 1 mv. between the electrodes.

It is inadvisable to clean the electrodes between titrations more than to wash them with distilled water. The small amount of selenium adher-

²¹ Moser, *Z. anal. Chem.*, **57**, 277 (1918).

²² Monnier, *Ann. chim. anal. appl.*, **20**, 1 (1915).

²³ Pleischl, *Kastner Arch.*, **93**, 430.

²⁴ Trautmann, *Bull. soc. ind. Mulhouse*, **61**, 87 (1891).

ing after the first titration increases the sharpness of the end-point. The coagulation of the colloidal selenium in the near vicinity of the end-point is quite distinct and affords a fairly close visual check on the titration.

Titration of Selenious Acid with Titanous Sulfate

Chemically pure selenium was dissolved in nitric acid, evaporated to dryness, and the selenium dioxide obtained purified by two sublimations. An approximately 0.05 *N* aqueous solution of selenious acid was prepared and standardized gravimetrically by reduction with hydrazine sulfate according to the method of Gutbier, Metzner and Lohmann.²⁵ In four experiments the weights of selenium obtained from 100.00 cc. of the solution were 0.0994, 0.0995, 0.0997, 0.0996 g., or an average of 0.0995 g.

TABLE XX

TITRATION OF SELENIOS ACID WITH TITANOUS SULFATE

Total initial volume in all cases, 100 cc.

SeO ₂ taken Cc.	Ti ₂ (SO ₄) ₃ required Cc.	Av. Cc.	Ti ₂ (SO ₄) ₃ calc. from Fe factor Cc.	Ti ₂ (SO ₄) ₃ calc. from KMnO ₄ factor Cc.
10.00	6.85			
10.00	6.75	6.80	6.70	6.72
15.00	10.15			
15.00	10.17			
15.00	10.18	10.15	10.05	10.08
15.00	10.10			
20.00	13.52			
20.00	13.52	13.52	13.40	13.44
30.00	20.15			
30.00	20.26			
30.00	20.15	20.19	20.10	20.16
30.00	20.20			
40.00	26.80			
40.00	26.80	26.80	26.80	26.88

The solution was, therefore, 0.0503 *N*. The purity of the selenium dioxide was 99.1%, the rest being, doubtless, moisture.

Samples of this solution were titrated electrometrically with titanous sulfate²⁶ in solutions containing 40% of conc. hydrochloric acid and saturated with sodium chloride. All titrations were conducted in a current

²⁵ Gutbier, Metzner and Lohmann, *Z. anorg. Chem.*, **41**, 297 (1904).

²⁶ Prepared by the electrolytic reduction of titanous sulfate and stored in an atmosphere of hydrogen. Thornton and Chapman, *J. Am. Chem. Soc.*, **43**, 91 (1921).

of carbon dioxide.²⁷ The titanium solution was standardized against a solution of ferric sulfate,²⁸ prepared from electrolytic iron of known purity, and against potassium permanganate.²⁹ Against the former it was found to be 0.0750 *N*, against the latter, 0.0748 *N*.

From a comparison of the volumes of titanous sulfate used in the several determinations it is evident that the excess of the titrating solution required to give the end-point reaction was very close to 0.10 cc. (The titrations with the 40.00cc. samples were evidently a little low.) When this correction is made, the check with the amount of titanium calculated from the iron factor is usually within 0.02 cc. The titration of the selenious acid proceeds, then, according to the equation: $\text{SeO}_2 + 4\text{HCl} + 4\text{TiCl}_3 = \text{Se} + 4\text{TiCl}_4 + 2\text{H}_2\text{O}$. There can be, therefore, no secondary reaction such as found by Moser²¹ and no empirical standards are necessary in the determination.

Effect of Varying the Concentration of Hydrochloric Acid

The effect of varying the hydrochloric acid concentration is shown in Table XXI.

²⁷A convenient arrangement for titrating in an atmosphere of carbon dioxide is shown in the sketch.

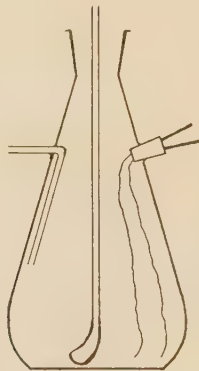


Fig. 17.

The platinum electrodes are slipped through a small 2-hole rubber stopper and inserted into a hole made about $\frac{1}{3}$ the distance down from the mouth of a 500cc. Erlenmeyer flask equipped with a gas inlet. The inlet tube must not dip below the surface of the solution.

²⁸ Titrated to the disappearance of the color of ferric thiocyanate. Thornton and Chapman, Ref. 56.

²⁹ Titrated by adding it to the permanganate in sulfuric acid solution. The permanganate was standardized against sodium oxalate from the Bureau of Standards.

TABLE XXI
EFFECT OF HYDROCHLORIC ACID
Total initial volume in all cases, 100 cc.

SeO ₂ taken Cc.	Ti ₂ (SO ₄) ₃ required Cc.	Vol. of HCl (Sp. gr. 1.18) in 100 cc. of soln. Cc.	Character of end-point
15.00	11.44	75	Very good. Fall at end-point not permanent but definite
15.00	11.40	50	Rise and fall extremely sharp
15.00	11.42	35	Very good
30.00	22.77	35	Very good
15.00	11.43	25	Rise more marked than fall
30.00	22.70	25	Good
20.00	15.08	25	Good
10.00	7.53	25	Good
15.00	...	10	Poor

An acidity of 25 to 75 cc. of conc. hydrochloric acid in 100 cc. of solution is entirely satisfactory.

Effect of Sulfuric Acid

In the preparation of an actual sample of metallic selenium for analysis it is very desirable to avoid the use of hydrochloric acid for removing the nitric acid in which the material is dissolved. In hydrochloric acid solution selenium chloride is appreciably volatile at the boiling point. For this reason the effect of sulfuric acid upon the titration was studied.

TABLE XXII
EFFECT OF SULFURIC ACID

15.00 cc. of 0.05 N selenious acid solution was used in each titration. The solutions were saturated with sodium chloride and had an initial volume of 100 cc.

Ti ₂ (SO ₄) ₃ Cc.	Vol. of conc. acid ^a in 100 cc. of soln. Cc.	Character of end-point
11.37	50 HCl	(Control titration)
11.40	50 HCl + 5 H ₂ SO ₄	Rise long and marked, fall slow. Titrated to end of rise
11.40	50 HCl + 10 H ₂ SO ₄	Not quite as good as the preceding. No permanent fall. Not difficult to determine end-point

^a Refers to HCl, d. 1.18, or to H₂SO₄, d. 1.84.

The acid may be present in amounts up to 5 or 10 cc. per 100 cc. of solution but is to be avoided in any considerable quantity.

The non-volatility of selenium in hot sulfuric acid was shown by the evaporation of samples of the selenium solution with 5 cc. of conc. sulfuric acid until dense fumes formed and then titration after the addition of sodium chloride and hydrochloric acid. The maximum variation was 0.06 mg. in a total of 15 mg., or 0.4%. The end-point, however, was not quite as sharp as when the fuming had been omitted.

Effect of Tellurium

Of the common associates of selenium, tellurium is probably of the greatest interest in its effect upon the titration of the former element. In a hot hydrochloric acid solution of moderate concentration tellurium is rapidly reduced by titanous salts, but in the cold the reduction, if any takes place, is very slow.

Metallic tellurium was carefully freed from selenium by Keller's method,³⁰ reprecipitated as metal, again dissolved in nitric acid, evaporated to fumes of sulfuric acid and dissolved in hydrochloric acid. Various amounts of this solution were added to known amounts of selenious acid solution and determinations made as outlined in Table XXIII.

TABLE XXIII
EFFECT OF TELLURIUM

15.00 cc. of 0.05 N selenious acid was used in each titration. Total initial volume, 100 cc.

Ratio, wt. Te:wt. Se	Ti ₂ (SO ₄) ₃ Cc.	Vol. of HCl (Sp. gr. 1.18) in 100 cc. of soln.	Character of end-point
...	11.34	50	(Control titration)
4:5	11.33	50	Sharp rise, no fall with excess
4:5	11.35	50	Regular fall with excess
8:3	11.35	50	Distinct rise, no fall with excess
4:1	11.35	50	No fall with excess
8:1	11.35	50	No fall
8:1	11.30	25	A fall
8:1	11.35	25	A fall
8:1	11.35	25	No fall. End-point a change in rate of rise

Tellurium even in large amounts does not interfere in the titration of selenium but it seems to affect the character of the end-point much as does sulfuric acid. The fall in potential as the end-point is passed does not always occur, but the rise is fully as sharp as in the absence of these substances. There is no difficulty in recognizing the completion of the reaction.

Effect of Iron

One of the most surprising and interesting things in connection with the selenium determination is the fact that the volume of titanium solution used in titrating mixtures of selenium and ferric iron is identical with that for the selenium alone although ferrous iron is formed during the precipitation. The character of the end-point is much the same as that described later with mixtures of selenium and copper, but no second end-point is obtainable at the point of complete reduction of both elements.

³⁰ Keller, *J. Am. Chem. Soc.*, **19**, 771 (1897). Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd ed., 1922, p. 423.

In Table XXIV the solutions contained 30.00 cc. of conc. hydrochloric acid in a volume of 100 cc. and were saturated with sodium chloride.

The behavior of selenium under these conditions seemed at first paradoxical. It was observed, however, that with large amounts of iron the precipitation was apparently incomplete. From two samples, one of which contained twice as much ferric iron as the other, the selenium was filtered at the end of the titration, thiocyanate was added, and more of the titanous solution run in. No sharp color change occurred. The deep red faded slowly only to reappear in a few seconds. The amount of titanium required for an approximate end-point was twice as much in the solution

TABLE XXIV
EFFECT OF IRON

SeO ₂ taken Cc.	0.05 N Fe ⁺⁺⁺ added Cc.	Ti ⁺⁺⁺ req. Cc.	Remarks
15.00	..	10.60	
15.00	1	10.58	
15.00	5	10.52	
15.00	10	10.61	
30.00	1	21.25	
30.00	10	21.26	
SECOND SERIES			
15.00	..	10.15	
15.00	25	10.22	Pptn. very incomplete
15.00	35	10.17	Pptn. very incomplete
15.00	50	10.15	Pptn. slight
30.00	50	20.20	Pptn. greater than preceding
10.00	75	6.82	No pptn. End-point a little slow

containing double the amount of iron. After much more titanous sulfate had been added there was a further precipitation of selenium. It appeared that ferric iron and selenious acid might form a rather unstable compound in which the selenium is reduced only with difficulty, requiring a large excess of titanium. An amount of ferric iron equivalent to the combined selenium is reduced along with the free selenious acid and the numerical result of the titration, therefore, is unaffected. In the second series the amount of iron was increased until no precipitation occurred, without affecting the results, thus supporting this view. The exact composition of the compound was not investigated.

Effect of Copper

In hydrochloric acid solution trivalent titanium reduces cupric salts to the cuprous form.³¹ When present with selenium, however, the latter is

³¹ Rhead, *J. Chem. Soc.*, **89**, 1491 (1906). Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918. Moser, *Chem.-Ztg.*, **34**, 1126 (1912). Monnier, *Ann. chim. anal.*, **21**, 109 (1916). Mach and Lederle, *Landw. Vers. Sta.*, **90**, 191 (1917). Thornton, *J. Am. Chem. Soc.*, **44**, 998 (1922).

reduced first and apparently selectively. The electrometric titration gives two end-points, one when the selenium is entirely precipitated and a second at the completion of the reduction of the copper. Toward the end of the first reaction the voltage starts to rise slightly. There is then a long, distinct, upward swing that marks the end-point, followed usually by continued rise. The copper end-point is a second sharp rise.³² It is not quite as clear as the first but readily distinguishable after a little experience.

Table XXV records a number of titrations carried out in the presence of copper.

TABLE XXV
EFFECT OF COPPER

All solutions titrated had an initial volume of 100 cc., contained 30–40% of conc. hydrochloric acid and were saturated with sodium chloride.

SeO ₂ taken Cc.	0.05 <i>N</i> CuSO ₄ added Cc.	Ti ⁺⁺⁺ req. for Se end-point Cc.	Total Ti ⁺⁺⁺ used Cc.	Ti ⁺⁺⁺ req. for Cu Cc.
...	5.00	...	...	3.55
15.00	..	10.50	...	..
15.00	..	10.50	...	..
15.00	5.00	10.53	14.02	3.49
15.00	10.00	10.50	17.60	7.10
15.00	1.00	10.52	...	..
SECOND SERIES				
15.00	..	10.65	...	..
15.00	5.00	10.65	...	..
30.00	5.00	21.24	...	..

Summary

1. The volumetric reduction of selenious acid to selenium by titanous sulfate is rapid and accurate to within 0.1 mg. in cold hydrochloric acid solution saturated with sodium chloride.

2. Under these conditions tellurium is not reduced and its only effect is to modify the nature of the end-point.

3. Moderate amounts of sulfuric acid have no deleterious effect upon the determination of the end-point and there is no volatilization of selenium at the fuming temperature in this acid.

4. The titration of selenium is quantitatively independent of the concentration of iron, although ferrous iron is formed in the reaction.

5. The reducing effect of trivalent titanium upon mixtures containing copper and selenium is selective, the latter being reduced first, and both elements may be determined in a single titration.

³² It is obvious that the method may be adapted to the determination of copper alone. A number of very accurate titrations were made in this way but this application is not stressed because of the rather large amount of other work on this reaction already published.

THE ELECTROMETRIC TITRATION OF MOLYBDENUM WITH A TITANOUS SALT

Introduction

The reduction of molybdic acid to a salt of pentavalent molybdenum by means of trivalent titanium was observed by Knecht and Hibbert.³³ They failed in the attempt to base a volumetric method for the determination of molybdenum upon this fact because of the lack of a suitable indicator for the end-point. An investigation of the applicability of the electrometric titration showed that the reaction is sufficiently rapid for this to be used. The character of the end-point with the polarized bimetallic electrode system with platinum electrodes is essentially as has been described for other titrations. After enough of the titrating solution has been added for equilibrium to be established, there is practically no further change until within about 0.5 cc. of the end-point. The potential difference increases slightly, decreasing again on the addition of excess titanium. Normally the maximum is perfectly definite when the titration is carried out slowly as the end is approached so that equilibrium may be maintained. Otherwise a transient and irregular decrease in e.m.f. may occur before the reaction is quite complete. It is safest to add several drops more of the titanous solution after the supposed end-point has been reached to insure that the potential decrease is permanent and increasing. The reduction is not ideally fast. For this reason it is probable that a better end-point would be obtained with the usual monometallic electrode system. This point was not investigated.

The acid concentration of the molybdenum solution is an important factor; 5–10% by volume of conc. hydrochloric acid is the most desirable; too high a concentration weakens the reducing power of trivalent titanium appreciably. Sulfuric acid is unsatisfactory. Heat increases the velocity of the reaction but is unnecessary except in special cases.

Titration of Sodium Molybdate with Titanous Sulfate

An approximately 0.017 *M* solution of c. p. sodium molybdate was titrated with titanous sulfate³⁴ standardized by the method of Thornton and Chapman³⁵ against ferric sulfate prepared from electrolytic iron of known purity.

³³ Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918, p. 99.

³⁴ Prepared by the electrolytic reduction of titanous sulfate and stored in an atmosphere of hydrogen.

³⁵ Thornton and Chapman, *J. Am. Chem. Soc.*, **43**, 91 (1921).

TABLE XXVI

TITRATION OF PURE SODIUM MOLYBDATE WITH TITANOUS SULFATE

The solutions contained about 8% by volume of conc. HCl and were heated to about 80°. 0.05 *N* Ti factor against Fe, 1.4002.

0.017 <i>M</i> Na ₂ MoO ₄ taken Cc.	0.05 <i>N</i> Ti ₂ (SO ₄) ₃ req. Cc.	0.017 <i>M</i> Na ₂ MoO ₄ taken Cc.	0.05 <i>N</i> Ti ₂ (SO ₄) ₃ req. Cc.
5.00	2.17	15.00	5.61
10.00	3.92	20.00	7.42

A finite excess of the titanous solution is required over that theoretically necessary for a reduction to the pentavalent state. This excess must be independent of the total amount of molybdenum present and may be determined by titrating solutions of varying molybdenum content and solving the equation, $n(a-x) = (b-x)$, where a and b are the number of cubic centimeters of the titrating solution required for 2 solutions of known molybdenum content, x is the required excess, and n the ratio of the weight of molybdenum in Solution b to that in Solution a .

Using the given formula, the excess of titanous solution required to give the end-point was determined from the data in Table XXVI. By combining Expt. 1 with Expts 2, 3, 4, x was found to be 0.42, 0.45, 0.42 cc., respectively; by combining Expt. 2 with Expts. 3 and 4, x was 0.54 and 0.42 cc.; by combining Expt. 3 with Expt. 4, 0.18 cc. was obtained. The average is 0.40 cc. The value of x is to some extent a function of the electrode system used and the magnitude of the polarizing voltage. For the most accurate results the titanium solution should be standardized against a molybdenum solution of known strength, using a volume of the titrating solution as nearly as possible equal to that required for the unknown. It was concluded from the results of a considerable number of titrations that an accuracy greater than 0.1 cc. of 0.05 *N* solution, which is the equivalent of 0.48 mg. of molybdenum, cannot be claimed for the method.

Titration of Molybdenum in Ammonium Phosphomolybdate

The titration of the molybdenum in a precipitate of ammonium phosphomolybdate is an excellent method of determining the phosphorus content of steels. No special refinements are necessary in standardizing the titanous solution for this purpose, since 37.11 mg. of molybdenum corresponds to 1 mg. of phosphorus and the effect of any slight error in the titration falls far below the limit of accuracy of the precipitation.

After precipitation of the phosphorus in the usual way³⁶ the ammonium phosphomolybdate is dissolved in ammonia, filtered to remove any iron, and the acidified solution titrated with titanous sulfate. If the precipitate is very large it tends to reprecipitate upon the addition of acid. This may be

³⁶ Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd edition, 1922, p. 365.

prevented by the addition of a few drops of phosphoric acid to the ammoniacal solution, but the character of the end-point is thereby altered. In the cold there is no voltage drop with excess of the titrating solution. Just preceding the end-point the normal rise begins, ceases, then continues with increased velocity just as the equivalent point is passed. If the solu-

TABLE XXVII
DETERMINATION OF PHOSPHORUS IN STEEL

Steel	Sample G.	H ₃ PO ₄ Sp. gr. 1.7 Cc.	Ti ⁺⁺⁺ req. Cc.	% P from Mo factor	% P from Fe factor	% P Certificate value
0.4 C.....	2.000	1	9.37	0.1016	0.1027	0.102
Bessemer.....	2.001	0	9.57	0.1016	0.1028	...
0.1 C.....	5.003	1	7.20	0.0312	0.0316	
B. O. H.....	5.002	0	7.22	0.0313	0.0316	0.031
	5.004	0	7.30	0.0316	0.0320	
0.1 C.....	2.003	0.5	10.31	0.1116		0.112
Bessemer.....	2.001	0.5	10.29	0.1100		

tion is titrated hot, however, the end-point is perfectly normal and as distinct as in the absence of the phosphoric acid. The separation of titanous phosphate sometimes occurs but has no effect upon the sharpness of the end-point.

Three Bureau of Standards steels were analyzed by this method; the results are shown in Table XXVIII. The 0.05 *N* factor of the titanium solution against molybdenum was 1.6765; against iron, 1.6956.

The color of the reduced solution is an extremely intense bluish purple and forms an excellent qualitative test for molybdenum even in amounts less than 1 mg. in the absence of tungsten and vanadium.

Effect of Tungsten

One of the most interesting points in connection with the molybdenum titration is the non-interference of tungsten even when present in large amounts. If anything, the end-point is rendered more distinct. Certainly, results seem to be more uniform. There is greater necessity for proceeding slowly near the completion of the titration than when no tungstic acid is present. Very transient decreases in potential occur near the end-point as the titrating solution is added drop by drop but cease just before the reaction is complete, and the permanent end-point drop is very distinct. The color is as characteristic as that of the complex phosphate, and is due to an intense blue-black, finely divided precipitate or a solution in case phosphoric acid is also present.

Various amounts of tungsten, in the form of a solution of pure sodium tungstate, were added to 15.00cc. samples of sodium molybdate, and

the molybdenum was titrated. The molybdate was standardized gravimetrically;³⁷ the 0.05 *N* factor was 1.0005. The titanous solution was standardized against iron; 0.05 *N* factor, 1.2904. All samples contained about 5% of conc. hydrochloric acid and were titrated cold.

TABLE XXVIII

EFFECT OF TUNGSTEN

0.05 <i>M</i> $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ added Cc.	0.05 <i>N</i> $\text{Ti}_2(\text{SO}_4)_3$ req. Cc.	0.05 <i>M</i> $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ added Cc.	0.05 <i>N</i> $\text{Ti}_2(\text{SO}_4)_3$ req. Cc.
0	15.38	5	15.02
1	15.10	15	15.06
2	15.07	75	15.06

If the calculated excess of titanous solution, 0.40 cc. (p. 51), is subtracted from 15.38 cc. it leaves 14.98 cc. The results obtained in the presence of tungsten are in very fair agreement with this theoretical value.

Separation of Molybdenum from Iron

Two methods are in general use for the separation of molybdenum from iron prior to the determination of the former element in steels: (1) precipitation of molybdenum as sulfide from slightly acid solution³⁸ and (2) precipitation of iron as ferric hydroxide by pouring the acid solution into hot sodium hydroxide solution.³⁹ An attempt was made to use another method based upon the insolubility of lead molybdate in 2% perchloric acid. This gives a complete separation from chromium and vanadium. If no other strong acids are present precipitation is complete, but iron is always occluded to some extent and must be removed by treatment with sodium hydroxide, thus detracting from the value of the proposed method.

Synthetic steels were prepared from ferric nitrate and a standard solution of sodium molybdate. The calculated amount of 60% perchloric acid to form ferric perchlorate and 9 g. in excess was added to each of the samples and the solutions were evaporated until fumes were evolved. A partial dehydration of the molybdic acid occurs but this presents no difficulties. Chromium, if present, is oxidized and lead chromate, which is much less soluble than the molybdate, will later precipitate. After the evaporated samples were dissolved in water the chromic acid was reduced with a slight excess of ferrous perchlorate. The reduced solutions were heated to boiling and the molybdenum was precipitated by slowly add-

³⁷ Weiser, *J. Phys. Chem.*, **20**, 857 (1916).

³⁸ Johnson, "Chemical Analysis of Special Steels," John Wiley and Sons, 3rd Ed., 1920, p. 156.

³⁹ Ref. 36, p. 56.

ing to the boiling solution⁴⁰ a solution of 10 g. of lead perchlorate.⁴¹ The final volume was 300 cc. After the solutions had stood overnight they were filtered through Gooch crucibles, washed with 2% perchloric acid, then with water, and the precipitates dissolved in sodium hydroxide. The asbestos and ferric hydroxide were filtered off, the filtrates acidified with a 5% excess of hydrochloric acid, and titrated with titanous sulfate.

TABLE XXIX

DETERMINATION OF MOLYBDENUM IN SYNTHETIC STEELS

In all experiments 1 g. of iron and 0.0720 g. of molybdenum were added. The latter required theoretically 10.00 cc. of titanous solution. This solution was standardized against the standard molybdate solution.

Cr added Mg.	V added Mg.	Ti ⁺⁺⁺ req. Cc.	Error Mg. of Mo
0	0	9.95	-0.36
0	0	9.90	-0.72
20	0	10.00	0.0
20	5	9.98	-0.14
20	5	10.00	0.0

Summary

The reduction of hexavalent molybdenum to the pentavalent state by titanous salts is sufficiently rapid for employment of electrometric titration.

This gives a means of determining molybdenum in alkali molybdates accurate to within 0.5 mg. and, indirectly, phosphorus in the precipitate of ammonium phosphomolybdate. Tungstic acid presents no interference and it also eliminates the necessity of applying a correction for the excess titanous solution required to give the end-point.

⁴⁰ Lead molybdate precipitates immediately and completely in the cold in 5% perchloric acid in the absence of iron. The latter interferes in the precipitation. With large samples of steel, 2 g. or over, considerable boiling is required for complete precipitation. No precipitation at all occurs in the cold.

⁴¹ Made by dissolving the theoretical quantity of pure litharge in perchloric acid. The oxide was added slowly to the cold, dilute acid, heated to boiling, cooled and filtered.

THE ELECTROMETRIC TITRATION OF THE HALIDES IN THE PRESENCE OF ONE ANOTHER

I. The Determination of Total Halide by Titration with Silver Nitrate

The usual silver titration of the halides and thiocyanate can be made more accurate and simple by using the electrometric indicator.⁴² The break at the end-point with the bimetallic electrode system decreases in magnitude as the solubility of the silver salt increases and is, therefore, poorest in the titration of chloride. The end-point here is a slight rise followed by a slow fall in the potential difference between the 2 electrodes. The change is not as abrupt as in many cases but is perfectly distinguishable, especially after a little practice. Due to the very weak oxidizing potential of the solution to be titrated, the initial voltage is high and there is little change up to the immediate vicinity of the end-point. The electrodes should not be cleaned between titrations, as the inversion point increases in clarity with the first few successive titrations.

In order to test the accuracy of the electrometric method a strictly 0.1 *N* solution of chemically pure sodium chloride was titrated with a standard solution of silver nitrate, prepared from a nitric acid solution of pure metallic silver.⁴³ The electrode system consisted of 2 fine platinum thermocouple wires wound in a small, loose spiral and polarized with 0.5 volt through an external resistance of 100,000 ohms. Four 10.00cc. samples of the chloride solution were acidified with 5 to 10 drops of nitric acid, diluted to 80 cc. and titrated. The volumes of silver nitrate used were 18.59, 18.59, 18.58, 18.60 cc., or an average of 18.59 cc. The theoretical requirement was 18.59 cc.

With the reversed titration the end-point rise is more pronounced than the fall; 25.00cc. samples of the silver nitrate were diluted to 90 cc. and titrated with the standard chloride. Three titrations required 13.45, 13.45, 13.45 cc., or an average of 13.45 cc. which is the theoretical amount. Theoretical results are obtained regardless of the direction of approach.

II. The Direct Titration of Bromide

Norman McCulloch⁴⁴ developed a method for the determination of bromide in the presence of chloride based upon the selective oxidation of the

⁴² Behrend, *Z. physik. Chem.*, **11**, 485, 466 (1893). Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2**, 672, 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, 1919. Liebich, "Die potentiometrische Bestimmung von Chlor, Brom und Jod," *Dissertation*, Dresden, 1920.

⁴³ The silver used had been especially purified for atomic weight work.

⁴⁴ McCulloch, *Chem. News*, **60**, 259 (1889). Sutton, "Volumetric Analysis," J. and A. Churchill, London, 10th ed., p. 170.

former in the presence of hydrocyanic acid by manganic chloride, formed by adding a standard solution of potassium permanganate to a very large excess of manganous chloride. The excess of the manganic compound was reduced with potassium iodide and the excess of the latter titrated with potassium permanganate to the iodine chloride end-point, employing the usual chloroform indicator. Iodide, if present, is oxidized with the bromide.

In testing this method with a view to simplifying it, the iodide titration of the excess manganic chloride was found to give a good electrometric end-point, but the results were unsatisfactory. The reaction does not proceed regularly except under rigidly controlled conditions and the consumption of the oxidizing agent is in excess of that required by the simple reaction.

In order to avoid the necessity of having the oxidizing agent present in excess it seemed desirable to attempt a direct titration with permanganate in the presence of hydrocyanic acid. It is evident that the success of the proposed method depends upon the relative velocities of the reactions:

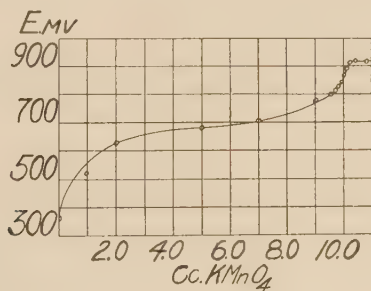
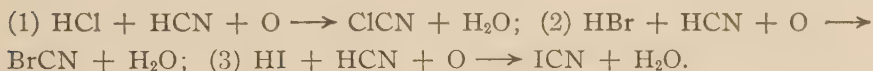


Fig. 18.—Titration of bromide in presence of chloride.

Pure potassium bromide was prepared by recrystallizing pure potassium bromate and fusing it in a platinum dish. A strictly 0.1 *N* (or 0.05 *M*) solution by weight was used in making the titrations recorded here. Hydrocyanic acid was obtained by adding a solution of chemically pure potassium cyanide (which gave no blank with permanganate), containing 100 g. of the salt per liter, to the acid halide solution prepared for analysis. Some of the titrations were carried out in an Erlenmeyer flask but the majority simply in an open beaker. The odor of hydrocyanic acid was distinctly noticeable but no serious discomfort was experienced during the course of a day's work.

The first titrations were run on solutions having an initial volume of 100 cc. and containing 10.00 cc. of potassium bromide solution, 5 cc. of

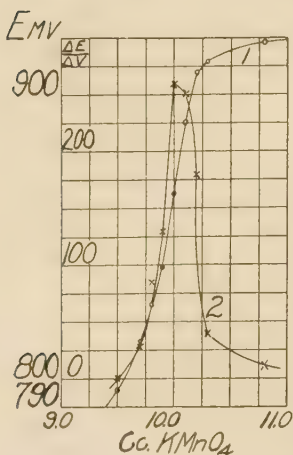


Fig. 19.—End-point in titration of bromide in presence of chloride.

potassium cyanide and various amounts of sulfuric and hydrochloric acids, using the bimetallic electrode system. No satisfactory end-point was obtained. The second reaction was a little too slow, or the first reaction too fast, or a combination of both, to give a sufficiently sharp potential break. For this reason the silver chloride electrode previously described⁴⁵ was substituted for one of the platinum wires and the titration curve plotted. Fig. 18 shows a typical titration curve.

The break is certainly not ideal, but offers distinct possibilities, particularly in a case such as this where there is no other method available. After each addition of permanganate there is a slight drag before equilibrium is reached but this is not serious although it is advisable to keep as uniform as possible the interval of time elapsing between adding the titrating solution and reading the buret. Ignition of the platinum electrode before each titration aids in keeping the end-point rise abrupt.

The data for the titration curve are given in Table XXX and the behavior in the near vicinity of the end-point is shown more in detail in Fig. 19.

TABLE XXX

TITRATION OF BROMIDE IN PRESENCE OF CHLORIDE

10.00 cc. of KBr; 5 cc. of KCN; 5 cc. of HCl (sp. gr. 1.19); 10 cc. of H₂SO₄ (sp. gr. 1.84).
Total vol., 100 cc.

KMnO ₄ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$	KMnO ₄ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$	KMnO ₄ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$
0.0	360	...	9.00	772	0	10.00	865	260
1.0	520	...	9.50	796	48	10.10	890	250
2.0	625	...	9.70	813	85	10.20	908	180
5.0	681	...	9.80	826	130	10.30	912	40
7.0	706	..	9.90	839	130	10.80	918	12

Theor. requirement, 9.91 cc.

Curve 1 was obtained by plotting the readings of the potentiometer against the corresponding buret readings; Curve 2, by plotting $\Delta E/\Delta V$

⁴⁵ This Thesis, page 12.

against V , the volume of titrating solution delivered.⁴⁶ The potassium permanganate used was standardized against pure sodium oxalate. Its 0.1 N factor was 1.0095. The theoretical requirement for this titration was, therefore, 9.91 cc. As nearly as can be read from the curve the flex in Curve 1 is at 10.00 cc. The maximum in Curve 2 is at the same point. The error is, then, 0.09 cc., which corresponds to 0.36 mg. of bromine.

Fig. 20 illustrates the end-point curve of a duplicate titration, which shows a different curve.

The results of several titrations are summarized in Table XXXI.

The theoretical permanganate requirement was 9.91 cc. in the first 5 titrations and 19.81 in the last 2. Particular attention should be drawn to the occurrence of a sub-maximum in Curve 2 of Fig. 20, since this is not always found. The succeeding decrease in the rate of the potential rise was at the theoretical end-point in both cases. The flex in the E - V curve is not easy to read with great accuracy; the maximum in the second curve is more readily determined. It may be observed that if an arbitrary correction of -0.10 cc. is added to this last value the error in the titration is never greater than 0.42 mg. of bromine. The amount of hydrochloric acid was increased in the fourth and sixth titrations to 10 cc. and in the fifth and seventh to 20 cc. without affecting the results. No sulfuric acid was used in the seventh titration.

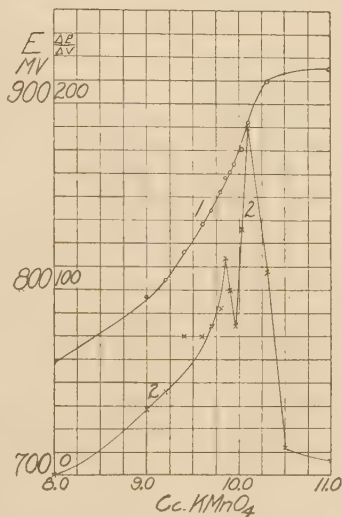


Fig. 20.—End-point in titration of bromide in presence of chloride.

TABLE XXXI

No.	Flex (Curve 1)	Maximum (Curve 2)	Minimum (Curve 2)
1 (Fig. 2)	10.00	10.00	..
2 (Fig. 3)	10.00	10.10	9.95
3	10.00	9.96	..
4	9.90	10.00	9.90
5	10.00	9.90	..
6	20.00	19.85	19.80
7	19.90	19.90	..

Effect of Iodide.—Iodide, if present, must obviously be titrated either with or before the bromide. A solution of potassium iodide was prepared and titrated with the standard permanganate. The end-point curve

⁴⁶ Hostetter and Roberts, *J. Am. Chem. Soc.*, **41**, 1341 (1919).

is shown in Fig. 21 and the data in Table XXXII. This titration will be discussed more fully later.



Fig. 21.—End-point in titration of iodide in presence of chloride.

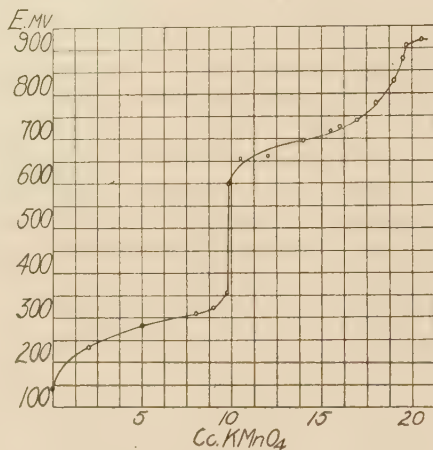


Fig. 22.—Titration of iodide and bromide in presence of chloride.

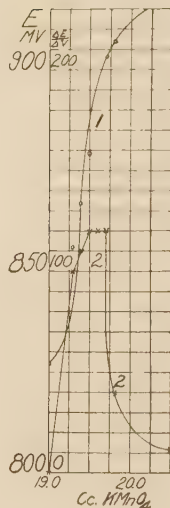


Fig. 23.—Final end-point in titration of iodide and bromide in presence of chloride.

TABLE XXXII

TITRATION OF IODIDE IN THE PRESENCE OF CHLORIDE

10.00 cc. of KI; 5 cc. of KCN; 10 cc. of HCl (sp. gr., 1.19); 10 cc. of H₂SO₄ (sp. gr., 1.84).
Total vol., 100 cc.

KMnO ₄ added Cc.	E Mv.	KMnO ₄ added Cc.	E Mv.	KMnO ₄ added Cc.	E Mv.
0.00	145	6.00	289	9.61 ^a	773
1.00	236	8.00	308	9.65	827
2.00	251	9.00	324	9.70	844
4.00	272	9.50	349	9.90	880
5.00	281	9.58	370	10.10	885
				11.00	900

^a End-point.

A duplicate titration gave identical results. When dealing with the pure iodide the break at the end-point is extremely great, about 400 mv.

The next step was to add the standardized iodide solution to known amounts of bromide and titrate the mixtures. Fig. 22 shows the curve

of such a titration and Fig. 23 the final end-point only. The data are given in Table XXXIII.

TABLE XXXIII

TITRATION OF BROMIDE IN PRESENCE OF CHLORIDE AND IODIDE

10.00 cc. of KBr; 10.00 cc. of KI; 5 cc. of KCN; 10 cc. of HCl (sp. gr., 1.19); 10 cc. of H_2SO_4 (sp. gr., 1.84). Total vol., 100 cc.

KMnO ₄ added Cc.	$\frac{E}{\text{Mv.}}$	KMnO ₄ added Cc.	$\frac{E}{\text{Mv.}}$	KMnO ₄ added Cc.	$\frac{E}{\text{Mv.}}$	$\frac{\Delta E}{\Delta V}$
0.0	142	9.79	365	17.0	741	...
1.0	235	9.83	380	18.0	777	...
2.0	251	9.85	600	19.00	827	0
5.0	282	9.95	650	19.30	856	97
8.0	309	10.5	655	19.40	867	110
9.0	323	12.0	661	19.50	979	120
9.5	338	14.0	695	19.60	891	120
9.68	348	15.5	717	19.70	903	120
9.75	356	16.0	725	19.80	907	40
...	...	...	...	20.50	916	13

Theoret. requirement, $9.61 + 9.91 = 19.52$ cc.

A sharp break occurred at 9.85 cc., 0.24 cc. higher than the iodide requirement. The solution turned deep red-brown as the permanganate was added but faded slowly to colorless in the vicinity of the end-point. The effect of the presence of bromide on the oxidation of iodide will be taken up under the discussion of the titration of the latter.

A duplicate titration gave similar results but the curve showed a sub-maximum as in Fig. 20.

These last two titrations may be summed up as follows: the flex (Curve 1) 19.42, 19.45; maximum (Curve 2) 19.50, 19.60; minimum (Curve 2) 19.50; theoretical volume of potassium permanganate, 19.52 cc.

Much the same conclusions may be drawn as in the preceding titrations. There is a tendency for the maximum in Curve 2 to occur too late. The submaximum was met with in only one of the determinations but then very close to the theoretical end-point.

Effect of High Concentration of Chloride.—It was apparent from the work so far that the presence of considerable amounts of hydrochloric acid offered no difficulties. In order to insure the entire non-interference of chloride under all conditions the regular bromide titration was now carried out in the presence of a very high concentration of pure sodium chloride. The samples contained 10.00 cc. of potassium bromide, 25 g. of sodium chloride, 5 cc. of potassium cyanide solution, and 10 cc. of conc. sulfuric acid in a volume of 100 cc. The titration curves showed no essential difference from those previously obtained.

Summarizing the results of three titrations: the flex (Curve 1) 9.95, 9.90, 10.00; maximum (Curve 2) 10.10, 9.95, 9.90; minimum (Curve 2) 9.90, 10.00.

The results are but slightly more irregular than with less chloride. Averaging the values for the maximum in Curve 2 and applying the correction adopted, -0.10 cc. of $0.1 N$ solution, give a permanganate consumption of 9.88 cc. This means a deviation from the calculated result of -0.03 cc., which is equivalent to 0.12 mg. of bromine. The maximum single deviation is 0.36 mg. of bromine.

III. The Determination of Iodide

A. The Determination of Iodide by Selective Oxidation with Permanganate to Iodine Cyanide

It was noted in connection with the determination of bromide that the oxidation of iodide was not far from being selective when the iodide and bromide were present in equal parts.⁴⁷ The iodide end-point was so remarkably distinct that it seemed worth while to investigate the possibility of adapting the same method to the titration of iodides.

As indicated by the titration curves⁴⁸ the oxidation of iodide is more rapid, the end-point break far greater, and sharper than with bromide. For this reason the bimetallic system is entirely satisfactory in this case and was used in all the titrations recorded here because of its greater simplicity. The break amounts normally to nearly 300 mv.

The first step was to determine the accuracy of the end-point inversion by titrating weighed samples of a standard solution of potassium iodide.

TABLE XXXIV
TITRATION OF IODIDE

Wt. of soln. G.	$0.1 N$ $KMnO_4$ used Cc.	I per g. G.
18.8481	37.35	0.012576
9.0338	17.95	0.012612
10.6316	21.14	0.012618
		Av. 0.012602

The samples were diluted to about 100 cc. for titration and contained 15 to 20 cc. of conc. hydrochloric acid and 5 cc. of a 10% solution of potassium cyanide. The results of three titrations are recorded in Table XXXIV.

This solution, standardized gravimetrically by precipitation as silver iodide, gave the value 0.012596 , which shows that the reaction proceeds

⁴⁷ See p. 65.

⁴⁸ See p. 64 Fig. 22

according to the equation, $\text{HI} + \text{HCN} + \text{O} = \text{ICN} + \text{H}_2\text{O}$, from which it follows that 1 cc. of 0.1 *N* potassium permanganate is equivalent to 6.346 mg. of iodine.

An approximately 0.1 *N* solution of potassium iodide was now prepared, standardized as above and samples of it were titrated in the presence of various amounts of the potassium bromide solution used in developing the preceding method. The acidity in all cases was 15% by volume of conc. hydrochloric acid.

TABLE XXXV

TITRATION OF IODIDE IN PRESENCE OF BROMIDE

Expt.	KI Cc.	0.1 <i>N</i> KBr Cc.	Ratio Br:I	Final vol. Cc.	KMnO ₄ used Cc.	Error Cc.
1	20.00	0	0	120	19.29	..
2	20.00	0	0	120	19.30	..
3	20.00	0.50	1:40	120	19.30	0.00
4	20.00	1.00	1:20	120	19.30	0.00
5	20.00	5.00	1:4	120	19.30	0.00
6	20.00	10.00	1:2	120	19.35	+0.05
7	20.00	20.00	1:1	120	19.48	+0.18
8	20.00	20.00	1:1	120	19.46	+0.16
9	10.00	10.00	1:1	120	9.75	+0.10
10	20.00	20.00	1:1	240	19.30	0.00
11	40.00	40.00	1:1	240	38.57	-0.01

Table XXXV clearly demonstrates that both the ratio of the concentrations of bromide and iodide and the absolute concentrations affect the accuracy of the titration. Until the ratio rose as high as 1:1 (Expt. 6) there was no interference in the titration of a 20.00cc. sample of the iodide. When the ratio reached unity the error was nearly four times as great (Expts. 7 and 8) but only twice as great as when the concentration was reduced by half (Expt. 9). Keeping other factors the same as in Expts. 7 and 8 but doubling the volume eliminated all error, while the error with this larger volume became negligible with the same absolute concentrations that in those experiments showed a large error.

It may be concluded that the selective oxidation of iodide to iodine cyanide by potassium permanganate in hydrocyanic acid solution is possible in all concentrations of chloride and in moderate concentrations of bromide, the magnitude of which is a function of the ratio of the concentration of bromide to the concentration of iodide and also of the absolute concentrations of each.⁴⁹ In cases where these factors are not known the

⁴⁹ After this work was ready for publication a paper appeared by R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922), in which he states that the oxidation of iodide to iodine cyanide in hydrocyanic acid solution is selective in the presence of chloride, bromide, and nitrate if the titrating solution is potassium iodate, but if potassium permanganate is used bromide interferes. It is desired to point out that Lang dealt with much higher concentrations of bromide than covered by our work.

proposed procedure is to titrate duplicate samples in dilutions varying by at least 100%. If the consumption of the oxidizing agent is the same in both solutions the results may be regarded as trustworthy.

Crotogino⁵⁰ and, later, Hendrixson⁵¹ developed a method for the selective oxidation of iodide in the presence of bromide and chloride by potassium permanganate based on a control of the acidity of the solution. Serious interference was encountered in the presence of much smaller amounts of bromide and chloride than are permissible in the method outlined here. Also, the break in Hendrixson's titration was only 160 mv. as compared with 400 mv. by the iodine cyanide method.

B. The Determination of Iodide by Oxidation to Iodate with Hypobromite

A method for the determination of iodide involving oxidation to iodate is, theoretically at least, the ideal method since the oxidation change is the greatest possible, and the presence of bromide and chloride in any amount cannot interfere.

It was observed that when a hypobromite solution was added to a neutral or alkaline solution of an iodide no change occurred at first, but after considerable hypobromite had been added the yellow color of the solution instantly faded.

An electrometric titration of the iodide with hypobromite was attempted but no end-point obtained. The results seemed to indicate that the oxidation of the iodide was complete but too slow for electrometric work.

An arsenite solution has no reducing effect upon an alkaline solution of iodate. It would, therefore, seem to offer an excellent possibility for a back titration of excess hypobromite added to an iodide solution.

TABLE XXXVI
TITRATION OF HYPOBROMITE WITH ARSENITE

KBrO taken Cc.	NaAsO ₂ req. Cc.	Average 0.1 N factor KBrO
5.00	4.20	
	4.20	0.8400
10.00	8.40	..
	8.41	0.8400
		Av. 0.8400

An exactly 0.1 N solution of sodium arsenite was prepared by weight from pure arsenious oxide dissolved in sodium carbonate. A solution of potassium hypobromite was made by pouring 40 to 50 g. of bromine slowly

⁵⁰ Crotogino, *Z. anorg. Chem.*, **24**, 255 (1899).

⁵¹ Hendrixson, *J. Am. Chem. Soc.*, **43**, 14, 859 (1921).

into a solution of about 30 g. of potassium hydroxide in 250 cc. of water, kept at nearly 0°, and diluting to 5 liters. This solution was standardized by titrating electrometrically with the arsenite.

The end-point with both mono- and bimetallic electrode systems is excellent. The bimetallic was used throughout the work here because of its greater convenience. The potential difference between the polarized electrodes increases slowly with the approaching end-point, the inversion is sharp and the subsequent fall unmistakable.

Weighed samples of a standard potassium iodide solution previously used (Table XXXIV) were rendered strongly alkaline with 1 g. of potassium hydroxide, an excess of potassium hypobromite solution, newly standardized, was added, the solution diluted to 100 cc. and allowed to stand for 5 minutes before titrating the excess hypobromite with arsenite (Table XXXVII). It was found by preliminary experiments that when the excess was titrated immediately, the results indicated that the oxidation of the iodide, especially when present in large amounts, was sometimes incomplete.

TABLE XXXVII
DETERMINATION OF IODIDE

Wt. soln. G.	0.1 N KBrO added Cc.	0.1 N NaAsO ₂ required Cc.	I per g. G.
7.9961	54.11	6.57	0.012574
5.2440	37.46	6.29	0.012571
6.4879	41.62	3.04	0.012577
7.2983	49.95	6.55	0.012577
6.6566	45.79	6.20	0.012579
2.8775	20.81	3.71	0.012569
			Av. 0.012575

The results in Table XXXVII agree well with those obtained gravimetrically, 0.012596, and by the iodine cyanide method, 0.012602 (Table XXXIV). Since 6 equivalents of oxygen are required in the oxidation to iodate, 1 cc. of 0.1 N hypobromite solution is equivalent to 2.115 mg. of iodine.

It is very evident that a solution of hypobromite can have no oxidizing action upon either a bromide or a chloride and exactly the same results were obtained in experiments in which 25 g. of sodium chloride and 10 g. of potassium bromide had been added.

The stability of a hypobromite solution depends largely upon the purity of the reagents used in its preparation.⁵² A high concentration of alkali also tends to retard decomposition. Unless the rate of decomposition is accurately known it is necessary to standardize the solution twice daily.

⁵² Willard and Cake, *J. Am. Chem. Soc.*, **43**, 1610 (1921).

Summary

1. The direct titration of bromide in hydrocyanic acid solution to bromine cyanide, BrCN , by potassium permanganate is too slow to be used with the bimetallic electrode system. If, however, the usual monometallic system is used and the titration curve plotted the end-point may be quite easily determined.

2. The oxidation takes place according to the theoretical requirement of 2 equivalents of oxygen, and the oxalate factor for the permanganate may be used. The maximum in the $\frac{\Delta E}{\Delta V} - V$ curve described usually lies a little too far to the right, but when a correction of -0.10 cc. of $0.1 N$ titrating solution is made the maximum error is less than 0.4 mg. of bromine.

3. A sub-maximum often precedes the end-point maximum in the $\frac{\Delta E}{\Delta V} - V$ curve and the intervening sub-minimum lies extremely close to the theoretical end-point. The sub-maximum does not always occur.

4. Iodide, if present, is oxidized to the corresponding iodine compound, ICN , but chloride in any quantity does not interfere. Since a selective determination of iodide is possible, the proposed method provides an excellent means for the rapid determination of bromide in the presence of any concentration of the other two halides.

5. Iodide may be accurately titrated electrometrically by oxidation to iodine cyanide with permanganate in hydrocyanic acid solution in all concentrations of chloride and in moderate concentrations of bromide.

The effect of bromide is a function of the ratio of its concentration to that of iodide and also of the absolute concentration of each.

6. A more accurate method is the oxidation of iodide to iodate by excess of alkaline hypobromite, the excess being titrated electrometrically with arsenite.

The presence of any amount of bromide or chloride is without effect.

Either the bimetallic or monometallic electrode system may be used in both methods.

THE ELECTROMETRIC DETERMINATION OF SULFUR IN SOLUBLE SULFIDES

Introduction

When the polarized bimetallic electrode system is used, the end-point in the electrometric titration of sodium sulfide⁵³ with an ammoniacal silver solution is unusually sharp. The e.m.f. rises slowly and sometimes irregularly at first, then there is a rise of 200 to 400 millivolts just before the end-point is reached, after which the completion of the reaction is marked by a very abrupt fall in potential. There is often a reversal of polarity during the titration which makes the first part of the rise apparently a fall. The proposed method is based upon the reaction used by Lestelle,⁵⁴ the precipitation of silver sulfide in alkaline solution by titration with standard ammoniacal silver solution. It is, however, much more simple and accurate than his visual determination of complete precipitation. The change in e.m.f. at the end-point is so great that it is never necessary to plot the curve.

Experimental Part

The sodium sulfide solution used in this work was prepared by absorbing 9 to 10 g. of hydrogen sulfide in a solution of 96 g. of sodium hydroxide and diluting to 6 liters. The titrating solution was a 0.05 *N* silver nitrate solution containing an excess of about 30 cc. of 28% ammonium hydroxide per liter and was standardized gravimetrically by precipitation of the chloride.

Samples of the sulfide solution were titrated in the cold, with an initial volume of 75 cc. The addition of more sodium⁵⁵ or ammonium hydroxide made no difference either in the quantitative or qualitative character of the end-point.

TABLE XXXVIII
ELECTROMETRIC TITRATION OF A STANDARD SULFIDE SOLUTION
10.00 cc. of Na₂S taken

0.05 <i>N</i> (NH ₃) ₂ Ag ⁺ req. Cc.	S in 10.00 cc. of Na ₂ S Mg.	0.05 <i>N</i> (NH ₃) ₂ Ag ⁺ req. Cc.	S in 10.00 cc. of Na ₂ S Mg.
18.05	14.47	18.02	14.43
18.04	14.46	36.05 ^a	14.45
18.07	14.48	...	Av. 14.46

^a 20.00 cc. of Na₂S taken.

⁵³ This is by no means the first attempt to utilize an electrometric indicator for detecting the completion of the precipitation of an insoluble sulfide. A number of workers have studied this end-point in various solutions and with different electrode systems but have met with rather doubtful success. Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2**, 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, 1919.

⁵⁴ Lestelle, *Compt. rend.*, **55**, 739 (1862).

⁵⁵ When insufficient sodium hydroxide is present the precipitate does not coagulate nor does the solution clear readily in the vicinity of the end-point.

The weight of sulfur in 10.00 cc. of this solution as determined by the Willard-Cake hypobromite oxidation method⁵⁶ was 14.48 mg., a variation of only 0.02 mg. from the average of the results obtained electrometrically. In Table LXIII a single titration of another solution showed a variation of 0.13 mg. from the value obtained by oxidation. Theoretically, the former method is 4 times as accurate as the latter since the ratio of the equivalents of sulfur in the two reactions is as 1 to 4 but in actual practice at least equal accuracy is claimed for the precipitation method, since it requires fewer operations and standard solutions and, incidentally, less time. The titrating solution is absolutely stable and can be very accurately standardized.

Effect of Sulfite

In taking up the effect of the more common impurities in the alkali sulfides, sulfite was the first to be investigated. Known amounts in the form of a solution of sodium sulfite were added to sulfide samples prepared for analysis. The final volume was 100 cc.

TABLE XXXIX
EFFECT OF SULFITE

10.00 cc. of Na_2S taken

SO_3^{--} added G.	0.05 N $(\text{NH}_3)_2\text{Ag}^+$ req. Cc.	SO_3^{--} added G.	0.05 N $(\text{NH}_3)_2\text{Ag}^+$ req Cc.
none	17.91	0.625 ^a	26.75
0.125	17.85	1.25	17.85
0.625	17.84	2.5	17.83

Av., all titr. in presence of SO_3^{--} 17.84
(Based on 10.00 cc. of Na_2S)

^a 15.00 cc. of Na_2S taken.

The sharpness of the end-point was not in the least impaired by the presence of various concentrations of sulfite. However, the titrations were slightly, but uniformly, lower than in the absence of this substance. It was concluded that this was due to a slight alteration in the nature of the end-point and not to any chemical effect. In any case the difference was only 0.07 cc., equivalent to 0.056 mg. of sulfur, which is negligible for all practical purposes.

Effect of Sulfate

The effect of the presence of sulfate upon the sulfide titration is shown in Table XL.

⁵⁶ Willard and Cake, *J. Am. Chem. Soc.*, **43**, 1610 (1921).

TABLE XL
EFFECT OF SULFATE

Sulfate was added to the sulfide samples as a solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The final volume in each case was 100 cc.

SO_4^{--} added G.	0.05 N $(\text{NH}_3)_2\text{Ag}^+$ req. Cc.	SO_4^{--} added G.	0.05 N $(\text{NH}_3)_2\text{Ag}^+$ req. Cc.
10.00 cc. of Na_2S taken	Titrated slowly	15.00 cc. of Na_2S taken	Titrated rapidly
none	17.80	none	26.47
0.12	17.74	0.6	26.42
0.60	17.72	2.4	26.42
1.2	17.63	...	...
2.4	17.61	...	...

The end-point was entirely normal in character. In the presence of sulfate, just as with sulfite, slightly less solution was required. In the first series this varied with the concentration of sulfate to a maximum of 0.19 cc. but in the second series, which was run more rapidly, this deficit was constant and amounted only to 0.05 cc., equivalent to 0.04 mg. of sulfur. It is believed that part, if not all of the apparent concentration effect was due to oxidation of the sulfide solution.

Effect of Chloride

Chloride did not interfere with the sharpness of the end-point even when present in large quantities but caused a more marked decrease than either sulfite or sulfate in the amount of silver required. This error in-

TABLE XLI
EFFECT OF CHLORIDE

Conc. NH_4OH added Cc.	Cl^- added G.	$(\text{NH}_3)_2\text{Ag}^+$ req. Cc.	Error due to end-point effect
First series. 10.00 cc. of Na_2S taken			
none	none	17.55	
none	0.1	17.46	
none	0.5	17.48	0.08 cc. = 0.06 mg. S.
Second series. 10.00 cc. of Na_2S taken			
none	none	17.46	
10	1.0	17.24	0.22 cc. = 0.18 mg. S.
10	2.0	17.13	0.33 cc. = 0.26 mg. S.
Third series. 15.00 cc. of Na_2S taken			
none	none	26.08	
10	2.0	25.77	0.31 cc. = 0.25 mg. S.

creased with the concentration of chloride but was somewhat decreased by the addition of ammonia to the sulfide solution probably because this increased the solubility of silver chloride.

Effect of Thiosulfate

The presence of thiosulfate rendered the potential drop with excess of the titrating solution less distinct but did not seriously affect the preceding rise nor the clarity of the end-point in general.

TABLE XLII
EFFECT OF THIOSULFATE

Thiosulfate was added as a solution of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The final volume was 100 cc.

$\text{S}_2\text{O}_3^{--}$ added G.	Vol. 0.05 <i>N</i> (NH_3) ₂ Ag ⁺ req. Cc.	$\text{S}_2\text{O}_3^{--}$ added G.	Vol. 0.05 <i>N</i> (NH_3) ₂ Ag ⁺ req. Cc.
10.00 cc. of Na_2S taken		15.00 cc. of Na_2S taken	
none	16.89	none	25.23
0.12	16.82	0.58	25.16
0.58	16.82	..	...
1.17	16.82	..	...
2.34	16.82	..	...

The deficit due to the presence of thiosulfate was 0.07 cc., the equivalent of 0.056 mg. of sulfur.

Effect of Polysulfide

A fresh solution of sodium sulfide was prepared and one portion of it shaken vigorously with pure, freshly precipitated sulfur from sodium thiosulfate in order to form polysulfide. Both solutions were titrated electrometrically and the total sulfur content was determined by hypobromite oxidation.⁶²

TABLE XLIII
EFFECT OF POLYSULFIDE

Sample Cc.	0.05 <i>N</i> (NH_3) ₂ Ag ⁺ req. Cc.	S in 10.00 cc. (elec.) Mg.	Total S in 10.00 cc. (by oxidation) Mg.	Difference Mg. S
10.00 Na_2S	23.53	18.86	18.73	+0.13
12.50 Na_2S	29.42	18.86		
10.00 Na_2S_x	23.52	18.85	19.44	-0.58
12.50 Na_2S_x	29.43	18.87		

Using the electrometric method no difference between the two solutions could be detected although the total sulfur content varied considerably, showing that only the sulfur present as normal sulfide is titrated.

Determination of Sulfur in Steel

To apply this titration to the determination of sulfur in steel, 2 samples from the Bureau of Standards were analyzed.

A 10g. sample of steel was placed in a 250cc. flask connected through a condenser to a hydrogen generator, a dropping funnel for admitting acid

and a "10-bulb tube" containing 100 cc. of a 10% sodium hydroxide solution. The apparatus was flushed out with hydrogen, 100 cc. of hydrochloric acid (sp. gr. 1.1) added and when the rapid evolution of hydrogen began to abate the solution was boiled. The stream of hydrogen was continued for 5 minutes after the steel had dissolved. The sodium hydroxide solution was washed into a beaker and titrated with standard ammoniacal silver solution. After the absorption process, the completion of the determination was a matter of only 2 or 3 minutes.

TABLE XLIV
DETERMINATION OF SULFUR IN STEEL

B. of S. Steel	Sample G.	S Found %	Certificate Value % S	
			Oxidation method	Evolution method
1.0% C	10.0000	0.026	0.027	0.028
B.O.H.	10.0034	0.026	...	...
0.1% C	10.0006	0.032	0.035	0.036
B.O.H.	10.0042	0.032	...	...

Summary

The electrometric end-point in the precipitation of sulfide by an ammoniacal silver solution is extremely sharp and gives a rapid and very accurate method for determining sulfide sulfur in the presence of sulfite, sulfate, chloride, thiosulfate and polysulfide.

THE ELECTROMETRIC DETECTION OF THE IODINE MONO- CHLORIDE END-POINT IN TITRATIONS EMPLOYING IODATE

Introduction

A number of analytical methods have been developed employing potassium iodate as an oxidizing agent in hydrochloric acid solution. In the presence of fairly conc. hydrochloric acid iodic acid reacts to form iodine monochloride, the end-point being determined by the disappearance of the violet iodine color when the solution is shaken with chloroform. Since the manipulation is sufficiently complex to render simplification desirable an investigation of the electrometric end-point was undertaken.

Andrew⁵⁷ showed that the oxidation of ferrous and antimonous chlorides, arsenious acid and iodide might be effected simply and accurately by potassium iodate. The method was later applied to thiocyanate by Jamieson, Levy, and Wells.⁵⁸ Because of the particular interest attached to this titration on account of its applicability to the determination of copper the reaction was selected for the proposed investigation. It is expressed by the equation



which shows that the theoretical equivalent of the thiocyanic acid is one-sixth of its molecular weight.

Experimental

An aqueous solution of pure potassium thiocyanate was prepared and compared with a standard solution of silver nitrate by the Volhard method and also electrometrically. The end-point with the bimetallic system is excellent, decidedly better than in the titration of chloride.⁵⁹ The results are recorded in Table 45.

TABLE XLV

STANDARDIZATION OF THIOCYANATE SOLUTION AGAINST SILVER NITRATE

KCNS taken Cc.	0.05 N. AgNO ₃ used Cc.	$\frac{M}{60}$ equiv. KCNS Cc.	$\frac{M}{60}$ factor KCNS
Titrated by the Volhard Method			
33.50	13.45	40.35	1.2045
40.15	16.14	48.42	1.2060
			Av., 1.2053

⁵⁷ Andrew, *J. Am. Chem. Soc.*, **25**, 756 (1903).

⁵⁸ Jamieson, Levy and Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

⁵⁹ This Thesis, page 60.

Titrated Electrometrically			
25.00	10.09	30.279	1.2111
25.00	10.08	30.246	1.2099
50.00	20.13	60.396	1.2079
50.00	20.15	60.460	1.2092
			Av., 1.2095

It may be observed that the electrometrically determined factor for the thiocyanate is a little higher than that found by the regular Volhard method, indicating the consumption of a greater volume of silver nitrate for a given titration in the latter case.

The usual bimetallic system gave an extremely good end-point when the thiocyanate solution was titrated with potassium iodate. The initial potential was low, beginning to rise slightly about 0.4 cc. before the completion of the reaction. The final break was very sharp, about 250 mv. during the addition of 0.02 to 0.03 cc. of the titrating solution. There was then no further appreciable rise or fall; the usual fall with excess of the oxidizing agent was absent.

A strictly $\frac{M}{60}$ solution by weight of potassium iodate, specially purified by two re-crystallizations, was used for titrating the thiocyanate solution. The final volume in all cases was 100 cc. and the concentrations of hydrochloric acid are expressed in per cent. by volume of concentrated acid (sp. gr. 1.18).

TABLE XLVI
TITRATION OF THIOCYANATE WITH POTASSIUM IODATE

KCNS Cc.	HCl % by vol.	Av. KIO ₃ Cc.	$\frac{M}{60}$ factor KCNS	Corrected vol. KIO Cc.	Corrected $\frac{M}{60}$ factor KCNS
10.00	25	12.10	1.2100	12.00	1.2000
20.00	25	24.10	1.2050	24.00	1.2000
10.00	15	12.10	1.2100	12.00	1.2000
20.00	15	24.10	1.2050	24.00	1.2000
10.00	10	12.10	1.2100	12.00	1.2000
20.00	10	24.11	1.2055	24.01	1.2005
10.00	5	12.20	1.2200	12.10	1.2100
10.00	5	12.15	1.2150	12.05	1.2050
20.00	5	24.18	1.2090	24.08	1.2040
20.00	5	24.30	1.2150	24.20	1.2100

* If Table 46 is considered quantitatively it will be observed that the results obtained were concordant until the concentration of hydrochloric acid fell to 5%. The consumption of potassium iodate then rose, irregularly, due to the hydrolysis of iodine monochloride. The factor for the thiocyanate checked those determination by both methods of silver titration but irregularly. It may be noted, however, that the iodate consump-

tion for 20 cc. always fell a little below the amount calculated from the value obtained for 10 cc. of thiocyanate. This can be due only to the necessity of the presence of a definite excess of iodate before the end-point phenomenon can be realized. This excess is clearly 0.10 cc. and if this correction is applied to the values in the third column the factors then obtained check perfectly but fall below that given by the Volhard method. This difference amounts to 0.0053 by the regular Volhard and 0.0095 by the electrometric silver titration method, or it is the equivalent of 0.3 mg. of copper per 100 cc. of $\frac{M}{40}$ titrating solution in the first case and 0.7 mg. in the second.

Summary

In a solution containing not less than 10% by volume of conc. hydrochloric acid, to prevent the hydrolysis of iodine monochloride, the electrometric end-point in titrations with iodate is very sharp. The results obtained in the determination of thiocyanates are slightly lower than those obtained by the Volhard silver titration method although it is evident that the break at the end-point occurs in the presence of a definite excess of iodate, for which a correction may be applied. The titration may be carried out more rapidly and accurately than with the usual chloroform indicator.

FURTHER APPLICATIONS

Besides the methods which have been developed here somewhat in detail there were a number of other titrations with the bimetallic electrode system which were less thoroughly investigated but which gave promise of further valuable applications. It is desired to mention some of these briefly.

Titration with Mercurous Perchlorate

Good results were obtained in the titration of iodide, bromide, chloride, and thiocyanate, in neutral or slightly acid solution with mercurous perchlorate. The end-points obtained were very similar to those given in the corresponding titrations with silver nitrate. Like the latter group of titrations the end-point improved with successive determinations so it is inadvisable to free the electrodes from the precipitate clinging to them between titrations. Simply washing them with water is sufficient. The chloride end-point is slow but may be somewhat improved if the titration is reversed.

A very brief investigation was made of the possibilities of titrating ferro- and ferricyanide with a mercurous solution. The end-point was not particularly sharp in either case but both determinations were possible. The ferrocyanide titration seemed the more favorable for development.

Mercurous perchlorate offers distinct advantages over any other mercurous salt for volumetric purposes. It may be readily obtained pure, is stable, and does not hydrolyze on dilution. The 0.1 N. solution used here was very readily made by dissolving 10.83 g. of pure mercuric oxide in 10 g. of perchloric acid, heating over metallic mercury, and diluting to 1 liter.

THE TITRATION OF MERCUROUS PHOSPHOTUNGSTATE

In connection with a study of the reaction between tetravalent vanadium and phosphotungstic acid it became necessary to determine the concentration of a given solution of the latter substance. It was found that the mercurous salt of the acid, precipitated with mercurous nitrate from a neutral solution according to the method of Gibbs,⁶⁰ could be titrated electrometrically with a standard solution of sodium bromide. The filter paper containing the carefully washed precipitate was placed in a beaker containing water or dilute nitric acid and the rapidly stirred suspension titrated directly with sodium bromide. The end-point was rapid and distinct.

TITRATIONS WITH SILVER NITRATE

The end-point in the titration of ferrocyanide was found to be improved if a standard solution of silver nitrate were substituted for the mercur-

⁶⁰ *Amer. Chem. Jour.*, **2**, 220 (1880).

ous perchlorate. The solutions titrated were slightly acid with nitric acid.

The electrometric titration of a neutral or slightly acid cyanide solution with silver nitrate was found to give an excellent end-point.

TITRATIONS WITH POTASSIUM FERROCYANIDE

Titration of Zinc

R. v. Bichowsky⁶¹ simplified the ferrocyanide method for the titration of zinc by substituting the regular monometallic electrometric apparatus for the uranium nitrate external indicator ordinarily used. Excellent results were obtained if the platinum electrode was properly pre-treated with ferrocyanide but the necessity of pre-treatment introduced an uncertain factor into the determination. The bimetallic system with its constant polarization potential was found to eliminate this last difficulty.⁶²

A 0.05 M. solution of chemically pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was prepared and titrated with a 0.025 M. solution of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. The data and end-point curve are given in figure 24.

On account of the irreversible character of the oxidation potential of Zn^{++} on platinum the initial potential difference is high. The end-point is marked by a fall in potential during the addition of a rather larger volume of the titrating solution than is the case in determinations employing a stronger reducing (or oxidizing) agent. The flex in the curve, or the point of maximum rate of change in potential, is not at all difficult to detect. It is entirely unnecessary to resort to plotting.

In order to check the end-point on multiple titrations a series of determinations was made. The results are recorded in the table.

TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE

ZnSO_4 taken 0.05 M. Cc.	$\text{K}_4\text{Fe}(\text{CN})_6$ used 0.025 M. Cc.	$\text{K}_4\text{Fe}(\text{CN})_6$ equiv. to 500 cc. ZnSO_4 Cc.
5.00	6.675	6.675
5.00	6.67	6.67
5.00	6.64	6.64
10.00	13.35	6.67
10.00	13.325	6.66
10.00	13.33	6.67
15.00	20.05	6.68
20.00	26.72	6.68

⁶¹ *J. Wash. Acad. Sci.*, **7**, 141 (1917); *J. Ind. Eng. Chem.*, **9**, 668 (1917).

⁶² Some work has been published on this titration since these experiments were made: I. M. Kolthoff, *Rec. trav. chim.*, **41**, 425 (1922). W. D. Treadwell and D. Chervet, *Helv. chim. acta*, **5**, 633 (1922).

Theoretically the requirement for the 5.00 cc. sample should have been 6.67 cc. The exact composition of the reagents used is somewhat open to question. Apparently no measurable excess of the ferrocyanide is required

10.00 cc. ZnSO_4
 3-4 g. NH_4Cl
 4.0 cc. HCl
 Initial vol., 75 cc.
 Titrated cold.

$\text{K}_4\text{Fe}(\text{CN})_6$ Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$
0.0	350	..
2.0	345	..
5.0	310	..
7.0	295	..
9.0	295	..
11.0	298	..
12.0	300	..
13.00	298	0
.20	300	10
.25	318	360
.28	295	-767
13.325	240	-1222
.37	204	-655
.40	195	-300
.50	175	-200
.60	165	-100

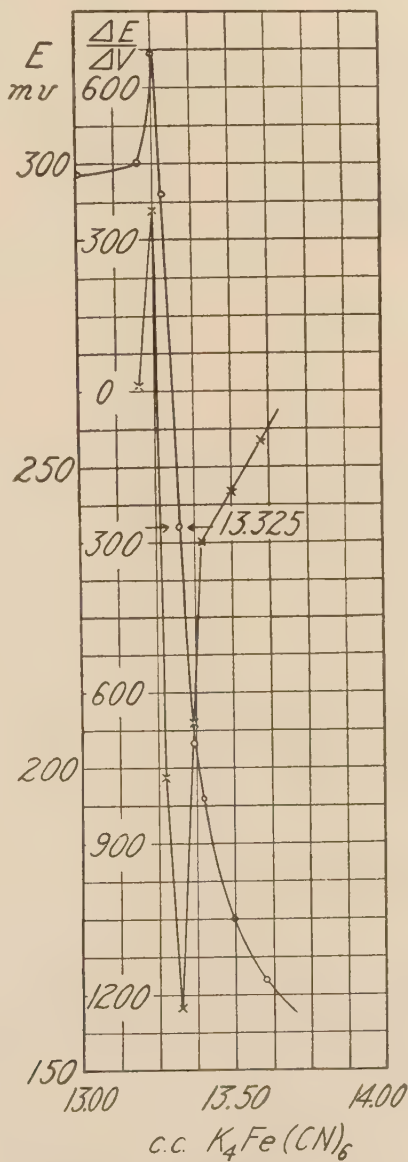


Fig. 24.

to give the end-point break and the reaction proceeds in entire agreement with the equation.

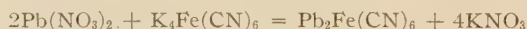


Titration of Lead

In acetic acid solution lead ferrocyanide is sufficiently insoluble to give an excellent electrometric end-point when a slight excess of ferrocyanide is added to a solution of a lead salt. The titration may be carried out more successfully in a cold solution than in a hot. The results of several titrations carried out in an approximately 0.05 M. solution of ordinary "C. P." lead nitrate with the 0.025 M. potassium ferrocyanide used above are given below.

TITRATION OF LEAD WITH POTASSIUM FERROCYANIDE			
Pb(NO ₃) ₂ taken Cc.	K ₄ Fe(CN) ₆ req. Cc.	K ₄ Fe(CN) ₆ equiv. to 12.50 cc. Pb(NO ₃) ₂ Cc.	Glacial acetic in initial vol. %
12.50	12.45	12.45	5
12.50	12.45	12.45	5
25.00	24.89	12.445	5

The results show that the reaction may be represented by the equation



No excess is required for the end-point. Ammonium acetate must be absent and the titration cannot be carried out at all in the presence of mineral acid.

Titration of Cobalt⁶³

Cobalt ferrocyanide is more soluble than the corresponding lead compound. If the ferrocyanide titration is carried out in a very dilute acetic acid the voltage falls in the region of the end-point with each additional drop of the titrating solution and returns to normal with decreasing velocity. An empirical period of depression or magnitude of swing of the galvanometer needle may be selected as marking the end-point but the method at best is empirical.

TITRATIONS WITH POTASSIUM CYANIDE

Titration of Copper

The electrometric end-point in the regular titration of copper with potassium cyanide is sharper than the color end-point. The actual magnitude of the break varies somewhat with conditions and is not large but the system is very sensitive. The following table shows a short series of titrations made on a 0.05 M. solution of copper sulfate in ammoniacal solution with a cyanide solution of unknown strength.

⁶³ Jamieson, *J. Am. Chem. Soc.*, **32**, 757 (1910).

TITRATION OF COPPER WITH POTASSIUM CYANIDE

CuSO ₄ taken Cc.	KCN used Cc.	Excess required for end-point ⁶⁴ Cc.
5.00	4.20	..
10.00	8.45	-0.05
15.00	12.72	- .06
20.00	17.00	- .05
		Av., -0.05

The necessary excess of the titrating solution is -0.05 cc., or the end-point is reached while there is yet a finite concentration of Cu^{++} in the solution.

Titration of Nickel

The nickel-cyanide reaction gives a very fair voltage change of 50 or 60 mv. The results of a series of titrations are tabulated below.

TITRATION OF NICKEL WITH POTASSIUM CYANIDE

0.05 M. NiCl ₂ taken Cc.	KCN required Cc.
15.00	10.78
15.00	10.77
30.00	21.52

The potassium cyanide solution was not the same as that used for the determination of copper. The solutions contained about 1% excess ammonium hydroxide, sp. gr., 0.90.

Titration of Cobalt

The corresponding cobalt titration gave no end-point at all.

THE TITRATION OF ZINC WITH SODIUM SULFIDE

The titration of zinc with a sulfide solution is not possible in either neutral or acid solution but in the presence of excess ammonium hydroxide a fair end-point is obtained.

TITRATIONS WITH SODIUM ARSENITE

Titration of Hypochlorite

The titration of an alkaline hypochlorite solution with sodium arsenite is very similar to the hypobromite titration which was used in the determination of iodide. The end-point is ideally sharp and accurate and the titration may be carried out with greater speed than is possible with the use of the iodide-starch paper ordinarily used in the analysis of bleaching solutions.

⁶⁴ Calculated from the equation $n(a-x) = (b-x)$ where a and b are the volumes of CuSO_4 taken for the two titrations, n is the ratio $\frac{b}{a}$ and x the required excess.

Titration of Bromate

Potassium bromate is rapidly reduced by arsenite in hydrochloric acid solution. The end-point is marked by the usual rise in voltage followed by a fall in the presence of an excess of the titrating agent. The table contains the results of a number of determinations.

TITRATION OF BROMATE WITH SODIUM ARSENITE				
$\frac{M}{60}$ $KBrO_3$ Cc.	Conc. HCl in final vol. %	$\frac{M}{60}$ $KClO_3$ Cc.	$\frac{M}{20}$ $NaAsO_2$ Cc.	Character of end-point
5.00	5	none	5.00	Good, a little slow
5.00	5	none	4.97	Good
5.00	5	none	4.99	Good
5.00	10	none	4.99	Faster than with more dilute acid
5.00	8	5.00	4.97	Good

The end-point increases in speed and sharpness with the concentration of hydrochloric acid but is readily obtainable in a concentration as low as 5%. The last experiment shows the possibility of titrating bromate in the presence of chlorate. In a low acid concentration the difference between the oxidizing potential of these two substances is sufficient for a selective titration of bromate.

In order to investigate the concentration effect more carefully a series of titrations were made in which bromate was added to the acid arsenite solution containing chlorate.

TITRATION OF BROMATE IN PRESENCE OF CHLORATE			
$\frac{M}{20}$ $NaAsO_2^{65}$ Cc.	Conc. HCl in final vol. %	$KClO_3$ G.	$\frac{M}{60}$ $KBrO_3$ Cc.
5.00	5	none	4.96
5.00	10	none	4.96
5.00	5	1	4.94
5.00	10	1	4.10

When the acidity rose as high as 10% considerable oxidation of the arsenite occurred but there is every reason to conclude that if the concentration of hydrochloric acid does not rise over 8% a selective titration of bromate may be made in the presence of any quantity of chlorate.

TITRATIONS WITH POTASSIUM BROMATE

Titration of Iron

The oxidation of Fe^{++} with bromate is slow but in the presence of a small amount of a cupric salt the velocity of the reaction is increased to such an extent that an excellent end-point is obtained. A high concentration of

⁶⁵ Not the same solution used for determinations in table immediately preceding.

hydrochloric acid is necessary, about 15–20% of concentrated acid gives ideal results. The end-point is very sensitive. The magnitude of the break is not great, about 30 or 40 mv., but the drop in excess is more than usually distinct, due to the appearance of free bromine.

Titration of Cerium

Another determination involving the use of potassium bromate as the titrating agent is that of cerium. A solution of cerous nitrate was made alkaline with sodium hydroxide, hydrogen peroxide added and the solution boiled to destroy all excess of the oxidizing agent. An excess of standard arsenite was now introduced, the solution acidified with a considerable excess of hydrochloric acid, and the excess of arsenite titrated with potassium bromate. No quantitative results were obtained because of the lack of a known cerium solution but the determination proceeded perfectly smoothly and with apparent success. The titration may be carried out more rapidly and the end-point is much more definite than with the direct permanganate oxidation method of Lenher and Meloche.⁶⁶

A SUGGESTED POSSIBILITY FOR THE TITRATION OF BISMUTH IN THE PRESENCE OF LEAD

In a slightly acid and hot solution trivalent titanium reduces bismuth salts rapidly to metal. Considerable work was done toward the development of this determination with but indifferent success. The velocity of the reduction falls just short of being sufficient to give a good and uniformly dependable end-point with the bimetallic system. It is believed, however, that with a monometallic system, where a high reaction velocity is not of such great importance, the titration would be entirely practicable. The presence of lead in any quantity has no effect upon the determination.

⁶⁶ *J. Am. Chem. Soc.*, **38**, 66 (1916).

